A Thesis on

REMOVAL OF ZINC, NICKEL AND COPPER IONS FROM WASTE WATER USING CHAR-A SPONGE IRON PLANT WASTE

Submitted by

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CERTIFICATE

This is to certify that the thesis titled "***Removal of Zinc, Nickel and Copper ions from Waste Water using char - A Sponge Iron Plant Waste***", submitted to the National Institute of Technology, Rourkela by **Miss. Deepthi Tirumalaraju**, Roll No. **609CH303** for the award of the degree of **Master of Technology (Research)** in Chemical Engineering, is a bona fide record of research work carried out by her under my supervision and guidance. The candidate has fulfilled all the prescribed requirements. The thesis, which is based on candidate's own work, has not been submitted elsewhere for a degree/diploma.

In my opinion, the thesis is of standard required for the award of a Master of Technology (Research) degree in Chemical Engineering. To the best of my knowledge, she bears a good moral character and decent behavior.

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ABSTRACT

Adsorption is a well known technology to address water solution problem typically for heavy metal pollution. Batch studies for individual heavy metals such as Zinc, Copper and Nickel was investigated using adsorbent, sponge iron plant waste. Surface modification of the adsorbent was achieved using HCl treatment. Surface characterization using proximate and ultimate analysis indicated improved in carbon content. FTIR, BET, SEM/ EDX, analysis further confirmed its surface modification. Batch studies were conducted to explore the influence of various parameters such as initial solution pH, adsorbent dosage, contact time, temperature etc. The optimum conditions obtained were 28min contact time, pH 7, adsorbent dosage 1g/L, and 25°C temperature for Zinc, 30min contact time, pH 6.5, adsorbent dosage 1g/L, 25°C temperature for nickel and 30 min contact time, pH 6, and temperature 25°C for copper.

Adsorption data obtained was fitted to various model equations such as Freundlich, Langmuir, Temkin etc; that suggest best fit to Langmuir isotherm model. The maximum adsorption capacity of zinc, nickel and copper from Langmuir isotherm were found to be 64.10mg/g, 14.08 mg/g and 11.79 mg/g respectively. The R_L values for initial concentration range 10mg/L-100mg/L were 0.92-0.54, 0.2 – 0.02 and 0.52-0.09 for Zn, Ni and Cu respectively that were within the favorable range ($0<R_L<1$). The necessary data obtained were interpreted kinetically by using pseudo first order, and pseudo second order rate kinetics. In all the cases the kinetics followed pseudo second order rate equation. The contact time variation experiments were used to study the rate-determining step in the adsorption process. Among the two diffusion models film diffusion was considered to be the rate controlling step in the adsorption mechanism because of its lower diffusion coefficients. The negative values of $\Delta G^{\circ}$and ΔH° indicate that the process was thermodynamically spontaneous and exothermic in nature.

In Co adsorption studies using batch experiments there was no significant effect on the adsorption of zinc due to the presence of nickel. In contrast, the removal of nickel decreased from 57.40% for the single-ion nickel solution to 48% in the presence of zinc co-adsorption.

The ability of SIP waste to adsorb zinc and nickel in a fixed bed column was investigated using Perspex fixed bed column. The effects of operating parameters such as bed height and flow rate were studied. The percentage metal adsorption increased from 40% – 62.05% and 31.23%-

56.43% for zinc and nickel respectively with increase in bed height form 5cm to 15cm. Increase in flow rate from 10mLmin^{-1} to 20mLmin^{-1} witnessed decrease in removal from 60.75% to 40.92% for zinc and 56.17% to 31.23% for nickel. At the end, an attempt has also been made to model the data generated from column studies using the empirical relationship based on Thomas model. From the results it was observed that Q_o values calculated from the Thomas model is close to the Q, exp values obtained experimentally for both zinc and nickel. The column regeneration studies were carried out for one adsorption–desorption cycle using the elutant 0.1N HCl. On the basis of the results, SIP waste can be economically and efficiently used as an adsorbent for the removal of metal ions from wastewaters.

1 INTRODUCTION

1.1 INTRODUCTION

Environmental pollution is the most gruesome ecological crisis to which the whole world is engrossed today. It is due to global rise in population and our hunt to lead comfortable life resulting in urban industrial technology revolution and rapid exploitation of natural resources by man, in short, population explosion. Now a days Water pollution is becoming great threat to mankind as most of our daily activities are related to water. Water is an essential natural resource, which is crucial for a variety of purposes. It is a vital constituent of all animal and vegetable matters. It is also a necessary ingredient of animal and plant life. Its uses include drinking and other domestic customs, industrial cooling, power generation, agriculture, transportation and waste disposal. There are mainly three types of water sources present, namely surface water, under river flow, ground water. Surface waters and ground waters are greatly affected by pollution. The industrial effluent containing heavy metals are the main source of pollution in these water bodies.

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Srivastava and Majumder, 2008). Rapid industrialization and urbanization has lead to excessive release of heavy metals into aquatic systems. Industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides galvanizing plants, stabilizers, thermoplastics, pigment manufacture, etc., discharge heavy metals and wastewaters directly or indirectly into the environment increasingly, especially in developing countries. Due to their toxicity and non-biodegradability they accumulate in food chain posing severe damage to living organisms and many heavy metal ions are known to be toxic or carcinogenic. Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium. Thus, treatment of industrial wastewater containing soluble heavy metals has become essential in order to increase the quality of water.

Zinc is an essential trace element being used in enzymatic reactions in humans (Gul, et al., 2009). Its extended and excessive ingestion often lead to toxic effects such as carcinogenesis,

mutagenesis and teratogenesis as a result of bioaccumulation (ATSDR, 1993). Intake of zinc ranging from 100 to 150 mg/day interferes with copper metabolism and causes low copper status, reduced iron function, red blood cell microcytosis, and neutropenia, reduced immune function, and reduced levels of high-density lipoproteins. There are other reported effects including lethargy, anemia, vomiting and dizziness (Oyaro et al., 2007). According to the WHO standards the maximum contamination level of zinc is 5.0 mg/L.

Nickel is one of the heavy metals, an essential constituent for both plants and animals with very low concentrations. Nickel exceeding its critical level might bring about serious lung and kidney problems besides gastrointestinal distress, pulmonary fibrosis and skin dermatitis (Borba et al., 2006). Moreover nickel is human carcinogen. According to the WHO standards the discharged level of nickel into surface waters is 0.02 mg L^{-1} [3].

Copper is an important engineering material with wide industrial application and is an essential factor for animal metabolism. Extensive intake of Cu causes hemolysis, hepatotoxic and nephro toxic effects vomiting, cramps, convulsions, or even death (Krishnamurthy and Vishwanathan, 1991; Paulino et al., 2006). The maximum contaminant level for copper in surface water is 1.3 mg/L (US EPA).

Considering the harmful effects of these heavy metals, it is essential to bring these heavy metals in the waste water to their permissible limits. Various conventional treatment techniques are available for the heavy metal removal from water and wastewater which includes hydrometallurgical techniques, oxidation, reduction, precipitation, electro dialysis, membrane filtration, flotation, ion exchange, reverse osmosis, and adsorption (Esalah et al., 2000;. Canet et al., 2002; Zouboulis et.al., 1997). Most of these processes suffer from high operating cost. Adsorption is one of the most versatile techniques for the removal of heavy metals from low concentration wastewater containing heavy metal. The adsorption process has many advantages such as low cost mainly due to utilization of industrial, biological and domestic wastes as adsorbent, low operational cost, ease of operation compared to other processes, re-usability of adsorbent after regeneration. On the other hand the high cost of activated carbon (AC) limits its use in adsorption. To evade the high cost of activated carbon so many varieties of low-cost adsorbents have been developed and tested to remove heavy metal ions. Different adsorbents typically used include modified flax shive (El-Shafey et al., 2002), rice husk ash (Srivastava et

al., 2006), waste biomass, waste activated sludge (Norton et al., 2004), wood sawdust Modified Sugarcane Bagasse (Pereira, et al., 2009) and Lignite (Pentari, et al., 2009). In spite of several investigations using different adsorbents still new adsorbents are sorted due to increasing demand for treatment of industrial effluents.

Some of the industrial solid waste materials are being used as adsorbents these days. One of such kind is the waste produced by sponge iron plant was used in the present study. Sponge iron plant waste is major source of dust pollution and it needs to be treated well before disposal. It has been found out that around 1.6-1.75 tonne of Fe, 1.2- 1.5 tonne of coal & 0.035 tonne of dolomite are required for production of one tonne of sponge iron. This results in production of 0.54 tonne of solid waste which includes 0.25 tonne of dust and 0.29 tonne of coal char. Due to non- availability of good grade of coal, the amount of char fines increases. The size of char varies in size of 0.5 mm to 3 mm thus becomes difficult to handle. Apart from this, it takes a lot of area for disposal. A 100 TPD plants requires 10 acres of land annually for disposal of solid waste (Patra et al., 2009).

In the present study the adsorption of zinc, nickel and copper ions from aqueous solution using surface modified sponge iron plant waste (char) as an adsorbent was investigated. Batch studies were conducted using synthetic zinc, nickel, and copper solution. The influence of pH, contact time, initial metal ion concentration, temperature and adsorbent concentration were investigated to optimize the conditions for maximum zinc, nickel, and copper removal. The experimental data obtained were calculated and fitted using adsorption isotherms, various kinetic models, and thermodynamic studies were conducted. Fixed bed column studies were conducted to determine their practical applicability. The effect of parameters such as flow rate and bed depth on the shape of the breakthrough curve was examined. Thomas model was used to evaluate and predict the adsorption performance and capacity of SIP waste for zinc and nickel adsorption in a fixed-bed column. Desorption and column regeneration of zinc and nickel adsorption was also investigated.

1.1.1 OBJECTIVE

The overall objective of the study is to reduce Zn, Cu & Ni concentrations in aqueous solution using an industrial waste (Sponge iron plant waste). The specific objectives are as follows:

- To characterize sponge iron plant waste.

- To optimize the process parameters involved in adsorption of heavy metals from waste water using the waste
- To evaluate the adsorption capacity and rate of mass transfer through batch and column studies respectively.
- To evaluate the regeneration capacity of the adsorbent.

2 LITERATURE REVIEW

Heavy metals are one of the most hazardous pollutants to the environment because of their higher toxicity and non-biodegradability even at trace concentrations. They are cumulative poisons which are capable of being assimilated and accumulate in food chain posing a severe damage to the plant and living organisms (Idris, et al. 2004). Heavy metals can enter water bodies by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater. Heavy metals such as lead, zinc, nickel, mercury, cadmium, copper, arsenic, cobalt, chromium, bismuth, ferrous etc. have been identified as poisonous to ecosystem and human health even present in traces.

2.1 ZINC

2.1.1 IMPORTANCE OF ZINC

Zinc metal and zinc alloys are very resistant to corrosion. Due to its extensive usage in electroplating, metal plating, chemical manufacturing industries, etc. the demand of zinc has been increasing globally. Important uses of zinc are in metal plating and galvanizing (for example in producing car bodies) and as an alloy in plumbing and central heating systems.

Zinc compounds also have an enormous range of useful properties and are used in a very wide range of products. Some important applications are specified below:

- In paint industry, zinc oxide used as a white pigment, zinc chromate used as a rust inhibitor.
- Zinc chloride used as an electrolyte in dry-cell batteries.
- Depleted Zinc-64 is used widely in the nuclear industry.
- Used as protective coatings for steel.
- Casting industries.
- Used as an alloying metal with copper to make brass.
- Used as chemical compounds in rubber and paints.
- Used as sheet zinc and for galvanizing iron.

- Zinc oxide used in ointments for burns and skin protection, zinc pyrithione used in anti-dandruff shampoos.
- Used in Lozenges.
- Zinc chloride used in the manufacture of artificial silk and in printing and dyeing textiles.

Apart from industrial uses zinc plays a vital role in human metabolism. It is essential for plants, animals, and microorganisms (Sugarman 1983; Prasad. 2008) and used by more than one hundred specific enzymes for their catalytic function (Cousins 1996). It helps in increase of immune system (Solomons 1998; Prasad A.S 1995), wound healing (Heyneman 1996), protein synthesis (Prasad A.S 1995), normal taste and smell (Prasad A.S 1997), and is needed for DNA synthesis (National Academy Press, 2001; Prasad 1995), and cell division (Prasad 1995). Zinc is stored in the brain, in specific synaptic vesicles by glutamatergic neurons (Bitanihirwe and Cunningham 2009) and can "modulate brain excitability"(Hambidge et al., 2007). It plays a key role in synaptic plasticity and so in learning (Nakashima and Dyck 2009).

2.1.2 HARMFUL EFFECTS OF ZINC

Zinc is an essential trace element used for enzymatic reactions in humans (Gul 2009) and its extended and excessive ingestion may lead to several toxic such as carcinogenesis, mutagenesis and teratogenesis as a result of its bioaccumulation (CONAMA, 2005). Its toxicity can occur in both severe and chronic forms. Intake of zinc ranging from 100 to 150 mg/day interferes with copper metabolism and causes low copper status, reduced iron function, red blood cell microcytosis, and neutropenia, reduced immune function, and reduced levels of high-density lipoproteins (Hooper et al., 1980). Ingesting 200–800 mg/day of zinc can cause abdominal cramp, nausea, vomiting, and loss of appetite, diarrhea, headaches etc (National Academy Press, 2001). There are other reported effects including lethargy, anaemia, and dizziness.

The AREDS have done a study by taking 80 mg per day of zinc in the form of zinc oxide for 6.3 years, on average have revealed that there was a significant increase in hospitalizations for genitourinary causes, raising the possibility that constantly high intakes of zinc harmfully affect some aspects of urinary physiology (Lomaestro and Bailie 1995). Zinc allied with other metals, such as lead, copper, and cadmium causes additional air pollution. The most general

effect caused by zinc air pollution is “metal – fume fever “which is as a consequence of the inhalation of zinc oxide fumes (NAPCA 1969).

2.1.3 SOURCES OF ZINC POLLUTION

The two major sources of zinc in to the aquatic systems are domestic and industrial discharges. The details of the discharges are given below.

2.1.3.1 INDUSTRIAL SOURCES

Most of the zinc pollution is caused by industries. Zinc is released from industries such as: coal-burning power plants, iron and steel industries, manufacturing processes involving metals; and atmospheric fallout (Denton, et al. 2001). Other sources are

- Electroplating industries.
- Pulp and paper industries.
- Rubbers manufacture industries.
- Pharmaceutical industries.
- Textile mills.
- Mining industries,
- Pharmaceutical industries
- Automobile emission, etc.

2.1.3.2 DOMESTIC SOURCES

- Zinc occurs naturally in many foods
- Some toiletries contain zinc - for example medicated shampoos with zinc pyrithione to control dandruff.
- Residues of zinc from zinc-plated cold water tanks leach into tap water and are flushed away when water is used.

2.1.4 DIFFERENT TECHNIQUES FOR ZINC TREATMENT

According to the WHO standards the maximum contamination level of zinc is 5.0 mg/L. The majority of the industries are discharging effluents containing zinc more than its permissible limit. Thus the removal of zinc from the industrial wastewater before releasing it has turn out to

be necessary. There are several convectional techniques available for the removal of zinc ions from wastewaters.

- Chemical precipitation.
- Ion -exchange.
- Membrane filtration.
- Electrochemical methods.
- Biological methods.
- Adsorption methods.

2.1.4.1 CHEMICAL PRECIPITATION

Chemical precipitation is an effective and widely used technique in industries (Ku and Jung, 2001) because of its ease of operation and being inexpensive.

Charerntanyarak (1999) worked with chemical coagulation and precipitation by lime to treat synthetic wastewater consisting of Zn at 450 mg/L. He examined that the optimum pH was more than then 9.5. Ghosh et al. (2010) employed electro- Fenton process and chemical precipitation to treat rayon industry waste water containing Zn^{2+} (32 mg/L). Results shown about 99-99.3% removal was achieved in the pH range 9-10 using lime precipitation. Chen et al., (2009) also used lime precipitation for removal of zinc containing 100mg/L. He found that about 99.37-99.6% removal was obtained with pH range 7-11. Alvarez et al., (2007) employed precipitation process to treat zinc at a 1.35mM. They found that 94% removal was achieved at pH 3 using H_2S as precipitant.

2.1.4.2 ION –EXCHANGE

Ion-exchange processes have been extensively used for removal of heavy metals from wastewater due to their advantages, such as high treatment capacity, high removal efficiency and fast kinetics (Kang et al., 2004). Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution (Alyüz and Veli, 2009).

(Alyüz and Veli, 2009) employed ion- exchange process using Dowex HCR S/S cation exchange resin was evaluated for removal of zinc from aqueous solutions. They found that the

process was pH-dependent and 98% removal efficiency was obtained at pH 6. They also investigated equilibrium distribution coefficient (*D*) 2.25×10^4 whereas separation factor α is 0.1029. Doula (2009) worked on clinoptilolite -Fe system for removal of Zn from drinking water. He observed that the system has a very good metal adsorption capacity and for many of the cases the treated water samples were suitable for human consumption or for agricultural use. Heikki (1999) tested the removal efficiency of zinc from metal plating industy on four chelating exchangers; which were Amberlite IRC 718, Duolite ES 467, Spheron Oxin, and oxine impregnated active carbon and on an inorganic sodium titanate exchanger. He found that all the five exchangers performed well with 99% removal efficiency.

2.1.4.3 MEMBRANE FILTRATION

Membrane filtration technologies were generally used in removal of heavy metals as they are highly efficient, can be easily operated and space saving. The membrane processes commonly used for metal removal from the wastewater are ultrafiltration, reverse osmosis, and electrodialysis.

Landaburu-et al., (2009) studied the removal of zinc from synthetic wastewater by MEUF (micellar enhanced ultrafiltration) using SDS. They observed that the removal is surfactant to metal molar ratio (S/M) dependent, and rejection coefficients up to 99% were achieved when the S/M was above 5. Huang et al., (2010) employed with Polysulfone membrane using SDS surfactant. They found that about 92-98% removal of zinc with 50mg/L initial zinc concentration. Ipek (2005) employed reverse osmosis process to remove zinc from aqueous solution. He found 98.9% removal at an operating pressure 1100kpa. Abbas et al., (2008) worked with electrolytic method for the removal of zinc from waste water using a flow-through cell with amalgamated copper screen cathode. They investigated that a flow-through porous electrode made of amalgamated copper screen can be an effective device in removal of Zinc from simulated effluents, and the concentration of Zn (II) was reduced to $5mgL^{-1}$ during recirculation times ranging from 100 to 190min, depending on the flow rate.

2.1.4.4 ELECTROCHEMICAL METHODS

Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state. Electrochemical wastewater technologies are

rarely used as they involve relatively large capital investment and the expensive electricity supply. However, with the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades (Wang et al., 2007b).

Kabdaslı et al., (2009) employed electro-coagulation using stainless steel electrodes for reduction of zinc from waste water originating from metal plating industry. Their study demonstrated that 100% removal was achieved with an applied current density 9 mA/cm^2 at pH 6. Casqueira et al., (2006) reported 96% removal of zinc at optimum pH 7, current density $8mA/cm^2$ by using electro-coagulation. Nafaˆa et al., (2004) investigated the performance of electro-coagulation, with aluminium sacrificial anode, in the treatment of Zn^{2+}containing wastewater. Belkacem et al., (2008) employed electro-filtration technique with aluminium electrodes to remove zinc from wastewater. They found 99% removal at optimum parameters.

2.1.4.5 BIOLOGICAL METHODS

The use of biological process for wastewater treatment containing heavy metal ions is a recent development although the technique has been widely used in chemical and pharmaceutical industries in a commercial scale. It is a very promising process in the removal of heavy metal contaminants. The major advantages of biosorption are its high effectiveness in reducing the heavy metal ions and the use of inexpensive biosorbents. Biosorption processes are particularly suitable to treat dilute heavy metal wastewater. In this process algal, bacteria, fungi, yeast etc are used as biosorbents.

Aminah and Babu, (2009) employed biosorption process using water hyacinth as biosorbent, to remove Zinc (II) from aqueous solution. They found the maximum removal at pH 5.4, adsorbent dosage 0.2g, initial metal concentration of 10 mg/L and the optimum time contact was at 90 minutes for initial concentration 5 mg/L and 210 minutes for initial concentration 10 mg/L. Artola and Rigola (1999) reported biosorption of zinc by sludge micro-organisms obtained from different steps of a conventional SWT plant. They found that the best types of activated sludge for the process to be thickened, anaerobic and dewatered sludge which removed up to 90–98% of metal when working at initial zinc concentration lower than 50 mg/l. The biosorption of Zn^{2+} by dried marine green macroalga (C. linum) was studied by Ajjabi and Chouba (2009). They found that the dried alga produced maximum 1.97 mmol/g uptake at the optimum particle size (100-

315 mm), biosorbent dosage (20 g/L) and initial solution pH 5. Lisa Norton et al 2004 employed biosorption process for the removal of zinc from aqueous solutions using biosolids. They found that the process was pH dependent with pH 4 being optimal.

Although all these wastewater treatment techniques can be employed to remove heavy metals, they have their intrinsic advantages and boundaries. As chemical precipitation is a simple and economical process, the heavy metals removal from aqueous solutions has been traditionally carried out by this process. But, chemical precipitation can be used only to treat high concentration wastewater containing heavy metal ions and it is ineffective when metal ion concentration is low. And chemical precipitation produces large amount of sludge to be treated with great difficulties.

Ion exchange has been widely applied for the removal of heavy metal from wastewater. On the other hand, ion-exchange resins must be regenerated by chemical reagents when they are exhausted and the regeneration can cause serious secondary pollution. And it is expensive, particularly when treating a large amount of wastewater containing heavy metal in low concentration, so they cannot be used at large scale.

Membrane filtration technology can remove heavy metal ions with high efficiency, but it is having demerits such as high cost, process complexity, membrane fouling and low permeate flux which limited their use in heavy metal removal.

Electrochemical techniques for heavy metal removal are considered as the most rapid and well-controlled that require fewer chemicals, provide good reduction yields and produce less sludge. But, electrochemical technologies involving high initial capital investment and the expensive electricity supply, this restricts its development.

The demerits of all the above process made to search for other process which can overcome all the difficulties in the above process. One of such kind is adsorption process.

2.1.4.6 ADSORPTION METHODS

Adsorption is as an effective and economic method for heavy metal wastewater treatment among all the techniques. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process. In adsorption process a single or a group of ions/compounds get accrued on the surface of another

solid or liquid. The substance on which the adsorption takes place is known as adsorbent and the substance, which gets adsorbed, is called adsorbate. Adsorption is classified into two types based on the extent of attraction between the adsorbent and adsorbate.

- ❖ Physical adsorption or vanderWaal's adsorption.
- ❖ Chemisorption.

In physical adsorption, the forces of attraction between the molecules of the adsorbate and the adsorbent are of the weak van der Waals' type. Because the forces of attraction are weak, the process of physisorption can be easily reversed by heating or decreasing the pressure of the adsorbate in gas adsorption and established rapidly. The heat of adsorption are low i.e. about 20 – 40 kJ mol^{-1}. In physical adsorption compound formation dose not takes place. Physical adsorption can be of two types, i.e., monolayer adsorption and multi-layer adsorption. In chemisorptions, the forces of attraction between the adsorbate and the adsorbent are similar to those of chemical bonds which are very strong. In this process, the heat of adsorption usually varies from 40 to 400kJ/mol. In this case surface compounds are formed. This process is related with significantly high activation energy and therefore termed as activated adsorption. It is moderately a slow process. Chemisorptions, in general, is an irreversible process because of strong electrostatic force of interaction between the adsorbent and adsorbate molecules.

Physical adsorption is very effective, particularly at a temperature close to the critical temperature of a given fluid. Chemisorption occurs usually at temperatures much higher than the critical temperature and by contrast to physical adsorption, is a specific process, which can only take place on some solid surface for a given fluid. Contrary to physical adsorption, chemisorption leads to monolayer adsorption. Under favourable conditions, both the processes can occur concurrently or alternately. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, this process is exothermic in nature.

The majority of the adsorbents used in the industrial process have complex porous structures that consist of different sizes and shapes of pores. The total porosity is typically classified into three groups: micro pores (diameter, $d<2$ nm), meso pores ($2<d<50$ nm) and macro pores ($d>50$ nm). In adsorption process the pore size is important. Because the size of micro pores are comparable to those of adsorbate molecules, all atoms or molecules of the adsorbent can interact with the adsorbate species. This is the basic difference between adsorption

in micro, meso and macro pores. As a result, the adsorption in micro pore is essentially a pore filling process in which the main controlling factor is the pore volume. Mesopores walls are formed by a large number of adsorbent atoms or molecules, and the boundary of the inter-phase has a discrete physical meaning. That means the adsorbent surface area has a physical meaning. In macro pores the adsorption forces do not occur all through the void volume, but they take place at a close distance from their walls. Therefore, the mono and multilayer adsorption take place successively on the surface of meso-pores and their final fill proceeds according to the mechanism of capillary adsorbent condensation. The basic parameters illustrate mesopores are: specific surface area, pore volume and pore size or pore-volume distribution. The mechanism of adsorption on the surface of macro pores is similar from flat surfaces. Adsorption on this surface is usually neglected as the specific surface area of macro-porous solid is very small. The capillary adsorbate condensation does not occur in macro pores (Saroj, 2007).

Adsorption is a technology that appears more technically and economically feasible. The advantages of adsorption over other technologies are that no additional sludge is produced, additional reagents to overcome high alkalinity are not needed, and the pH of discharged wastewater is unaffected Urano and Tachikawa (1991).The adsorption process has many advantages such as:

- Low cost of adsorbent.
- Easy availability of adsorbent.
- Utilization of industrial, biological and domestic wastes as adsorbent.
- Low operational cost.
- Ease of operation compared to other processes.
- Re-use of adsorbent after regeneration.
- Capacity of removing heavy metal ions over a wide range of pH and to a much lower level.
- Ability to remove complex form of metals that is generally not possible by other conventional method.
- Environment friendly, cost effective and technically feasible alternative due to utilization of biomaterials (Saroj, 2007).

Adsorption studies were carried out using a varity of adsorbents such as: Activated carbon, low cost adsorbents for biomass, waste sludge, rice husk, sugarcane bagasse, lignite etc.

Activated carbon (AC) adsorbents are widely used in the removal of heavy metal contaminants. It contains a large micropore and mesopore volumes which results in high surface area. Because of this it is widely used in commercial scale. A large number of researchers are studying the use of AC for removing heavy metals (Jusoh et al., 2007; Kang et al., 2008). Leyva Ramos et al, (2002) investigated adsorption of zinc from aqueous solution onto commercial activated carbons C, F-400, F-300 and Centaur HSL in a batch adsorber. They found that adsorption isotherm for Zn (II) was dependent on solution pH and maximum adsorption uptake was achieved at pH 7.

Due to the high cost of Activated carbon limits its use in adsorption. Many varieties of low-cost adsorbents have been developed and tested to remove heavy metal. Hasan Cesur and Nilg¨un Balkaya 2007 examined the removal of zinc (II) ions from aqueous medium by phosphogypsum. They found the maximum adsorption of the zinc (II) ions on the phosphogypsum was obtained at the pH values between 9.0 and 10.0 and observed that the adsorption equilibrium was reached in 40 min and the adsorption data fitted well to Freundlich model. The adsorption capacity of phosphogypsum for zinc (II) ions was determined to be 2.57 mg g^{-1}. Sachin and Gaikwad (2011) studied the removal of zinc from electroplating industrial wastewater using a cheap adsorbent, cork powder. They found 98% removal of zinc in synthetic wastewater whereas the removal percentage for the electroplating industrial wastewater was 91%. The optimum pH was 6. Bayat, (2002) investigated the removal of zinc from aqueous solution two different Turkish fly ashes (Afsin-Elbistan and Seyitomer). Results revealed that at pH 8 the maximum uptake was obtained. Among the two adsorbents he found that the fly ash with high calcium content (Afsin-Elbistan) as an effective activated carbon.

Apart from these adsorbents many low cost adsorbents from agriculture waste are also in use. El-Shafey (2010) used a carbonaceous sorbent prepared from rice husk via sulfuric acid treatment to remove zinc from waste water. He found Sorption of Zn (II) was extremely low at low pH values and increased with pH rising with a decrease in the final pH due to protons release in solution and E_a was found to be ~13.0 kJ/mol for Zn (II) sorption indicating a diffusion-controlled ion exchange mechanism. Olayinka et al., (2007) reported the use of waste tea,

coconut shell and coconut husk as potential low cost adsorbents for removal of Zn (II) from electroplating plant effulent. They observed that all the three adsorbents showed high rate of adsorption (cocunut shell, 99.74%, cocunut husk 99.76% and waste tea 90.74% removal).

Jang-Soon et al., (2010) studied removal of zinc from aqueous solutions by scoria (a vesicular pyroclastic rock with basaltic composition) from Jeju Island, Korea. They found up to 63% zinc removal after a reaction time of 24 h under a sorbate concentration of 1mM and the solution pH of 5.0. Pereira 2010 used new chelating material derived from wood sawdust, Manilkara sp., and chemically modified sugarcane bagasse synthesized to remove Zn^{2+} from aqueous solutions and electroplating wastewater. Zn^{2+} adsorption capacities were found to be 80 mg/g for ES and 105 mg/g for EB whereas for the industrial wastewater these values were found to be 47 mg/g for ES and 45 mg/g for EB. Shukla and Pai (2005b) batch adsorption studies to remove Zn(II) from waste water using Reactive Orange 13 modified Groundnut shells. The maximum uptake found was $9.57 mgg^{-1}$. sc´iban et al.,. (2006a) employed adsorption of zinc on to sodium hydroxide modified Sawdust (Poplar tree). The adsorption capacity was to be $15.8 mgg^{-1}$. Medhat (2007) reported the use of dried non-living biomass (NB) of different Pseudomonas strain as adsorbents to remove Zn (II) from waste water. He found optimum pH as 4.4 at which maximum metal removal was achieved.

2.2 NICKEL

2.2.1 IMPORTANCE OF NICKEL

Nickel is a metal of widespread distribution in the environment. There are almost 100 minerals of which Nickel is an essential constituent and which have many industrial and commercial uses. Not only for industrial use, but it is also an essential element for healthy animals, micro-organisms, plants and probably for humans. It is a versatile element and forms alloy with most metals.

Nickel and nickel alloys are used for a wide variety of applications, the majority of which involve corrosion resistance and/or heat resistance. Some important applications are specified below:

- Aircraft gas turbines.
- Steam turbine power plants.

- Medical applications.
- Nuclear power systems.
- Chemical and petrochemical industries.
- Making of austenitic stainless steel.
- Used as a catalyst in certain chemical reactions.
- Used in structural work and in electroplating.
- Used as an alloying element in ferrous alloys, low cost steels, cast iron etc.
- Rechargeable batteries, coinage, foundry products, and plating.
- In armour plates and burglar-proof vaults.

A number of other applications for nickel alloys involve are:

- Alloy alnico is used in magnets.
- In crucibles for chemical laboratories.
- Smart wire, or shape memory alloys are used in robotics.
- Monel metal, a copper-nickel alloy being highly resistant to corrosion is used for ship propellers, kitchen supplies, and chemical industry plumbing etc.

Apart from industrial applications nickel plays a crucial role in plant and micro organism metabolism (Astrid Sigel, 2008). Nickel is essential for plant growth (Brown, 1987). It is also an essential component of hydrogenases involved in nitrogen fixation and other associative bacterial processes, and it clearly influences plant response to disease.

2.2.2 HARMFUL EFFECTS OF NICKEL

Nickel is one of the heavy metal, which is an essential constituent for both plants and animals, but is required in very low concentrations. Extensive intake of nickel in large quantities has the following consequences:

- Higher chances of development of lung cancer, nose cancer, larynx cancer and prostate
- Cancer.
- Sickness and dizziness after exposure to nickel gas.
- Lung embolism.
- Respiratory failure.

- Birth defects.
- Asthma and chronic bronchitis.
- Allergic reactions such as skin rashes, mainly from jewellery.
- Heart disorders.
- Paranasal sinuses.
- Extra weakness etc (Al-Asheh and Duvnjak, 1997, Kadirvelu 1998, Beliles 1979).

Nickel fumes are respiratory irritants and may cause pneumonitis. Exposure to nickel and its compounds may result in the development of a dermatitis known as “nickel itch” in sensitized individuals.

2.2.3 SOURCES OF NICKEL POLLUTION

Majority of the nickel is discharged from industries and mining.

- Nickel miners, smelters and refiners.
- Nickel alloy manufacturers.
- Iron and steel industries.
- Electroplating industries.
- Batteries and metal plating.
- Insecticides and fungicides.
- Photography
- Electrical wiring.
- Smelting industries.
- Fertilizer industries.
- Nickel containing alloys such as in coinage in various forms of 'costume' or 'fashion' jewellery etc.

2.2.4 DIFFERENT TECHNIQUES FOR NICKEL REMOVAL

According to the WHO standards the maximum contamination level of nickel is 0.02 mg L^{-1}. The majority of the industries are discharging effluents containing zinc more than its permissible limit. Thus the removal of zinc from the industrial wastewater before releasing it has turn out to

be necessary. There are several convectional techniques available for the removal of zinc ions from wastewaters.

- Chemical precipitation.
- Ion -exchange.
- Membrane filtration.
- Electrochemical methods.
- Biological methods.
- Adsorption methods.

2.2.4.1 CHEMICAL PRECIPITATION

Naim, et al (20100 employed chemical precipitation to remove nickel from electroplating industry wastewater using three precipitating agent namely hydroxide, sulfide and carbonate. They found that sulfide precipitation was a viable option for the treatment of electroplating industry wastewater as compared to hydroxide and carbonate precipitation. Stephen et al, (2006) investigated removal of nickel from synthetic nickel plating wastewater using Sulfide and Carbonate for Precipitation and Co-precipitation. It was found that the optimum removal was achieved at pH 11 where a residual total nickel concentration of 0.1 mg/L was obtained with a sulfide: nickel weight ratio of 2.0 and a carbonate: nickel weight ratio of 20.0. Animes et al, (2008) reported the removal of nickel from plating rinse effluent using chemical techniques. They observed that Nickel concentration can be reduced below the discharge limit from the industrial plating effluent by chemical precipitation and coagulation at pH above 8. Papadopoulos et al, (2003) employed chemical precipitation to remove Ni (II) from waste water. They observed 85% removal at pH 10.5 with in 1 hr contact time.

2.2.4.2 ION- EXCHANGE

Argun, (2008) investigated the use of clinoptilolite ion-exchange resin in removal of nickel from wastewater. He conducted batch experiments at different varying the parameters and achieve 93.6 % removal at 7 pH, and adsorbent dose 15 g/L. Kumar et al., (2010) employed ion exchange process to remove nickel from aqueous solution using Ceralite IR 120 cationic exchange resin (CXR) as an adsorbent. They observed maximum Ni^{2+} removal at pH 5.0 and the

equilibrium was attained at 35 min.. Elshazly ,and. Konsowa (2003) reported the removal of nickel ions from wastewater polluted with nickel chloride using a cation-exchange resin in a stirred tank reactor. They found that mass transfer coefficient decreases with increasing nickel ion concentration and increases with increasing the degree of stirring and temperature and nickel ion removal rates up to 88.5% were obtained. Rodrıguez-Iznaga et al., (2002) used natural clinoptilolite from Caimanes deposit (Moa-Cuba) for the nickel removal from aqueous solution by ion exchange process. They tested stability of clinoptilolite as an exchanger for Ni^{2+} under hydrothermal conditions and high ammonia concentrations. No loss in the clinoptilolite exchange capacity of Ni^{2+} ions during the Ni^{2+} removal–elution cycles was observed.

2.2.4.3 MEMBRANE FILTRATION

Danisa and Aydiner (2009), employed ultra filtration process to remove nickel from wastewater by micellar enhanced ultrafiltration using Sodium lauryl ether sulfate surfactant. 98% removal was obtained at an optimum pH 7. Barakat and Schmidt, (2010) reported the use of polymer enhanced ultrafiltration (PEUF) to remove nickel from aqueous solution using Carboxy methyl cellulose complexing agent. Maximum removal (99.1%) was achieved at pH 7 and 10 mg/L initial metal concentration. Molinari et al., (2008) used PEI as a polymer to study the complexation-ultrafiltration process in the removal Ni (II) aqueous solution. From the Preliminary tests he found the optimal chemical conditions for Ni (II) complexation by the PEI as pH > 8.0, and polymer/metal weight ratio of 6.0.

(Mohsen-Nia et al., 2007) reported that Ni^{2+} ions were successfully removed by the RO process and the rejection efficiency of the ions increased up to 99.5% by using Na_2 EDTA at 5 atm operation pressures. Ipek, 2005, employed reverse osmosis process to remove nickel from aqueous solution. He found 99.3% removal at an operating pressure 1100kpa with initial metal concentration 44-169 mg/L. Galaya, and Poonpetch (2002) investigated membrane separation process using two membrane types, cellulose acetate microfiltration membrane with pore size 0.2 μm and polysulfone ultrafiltration membrane with MWCO of 30 kDa to remove nickel ions from electroplating wastewater. Experimental results showed the maximum rejection % (96.00-97.39) at pressure 50 kPa.

2.2.4.4 ELECTROCHEMICAL METHODS

Heidmann and Calmano (2010) tested the performance of an electro-coagulation system for Ni removal from a galvanic wastewater in laboratory scale. Results revealed that the best cleaning and the most effective removal could be achieved with a combination of Fe- and Al-electrodes and initial pH > 5.0. Kabdaslı et al., 2009 employed electro-coagulation using stainless steel electrodes for reduction of nickel from waste water originating from metal plating industry. Their study demonstrated that 100% removal was achieved with an applied current density 9 mA/cm^2 at pH 6. Heidmann and Calmano (2008) investigated the performance of an electro-coagulation process with aluminium electrodes for removing Ni^{2+}. They observed that the removal rates were not influence by the initial concentrations ranging from 50 mg/L to 5000 mg/L. Khelifa et al., (2005) employed electro-flotation process to remove nickel from wastewater. They found 98% removal at pH 6 with an applied current 0.3A

2.2.4.5 BIOLOGICAL METHODS

Parameswari et al, (2009) investigated the removal of nickel using *Azotobacter chroococcum, Bacillus* sp. and *Pseudomonas fluorescens* isolated from sewage effluent and sewage irrigated soils. The maximum nickel removal (84.32 % and 90.98 % by *A. chroococcum, Bacillus* sp. and *P. fluorescens* respectively) achieved was found to be 72 hr with an initial concentration of 25ppm. Shankar et al., (2007) employed biosorption process to remove nickel from industrial wastewater using heavy metal resistant fungi and bacteria isolated from the soil samples of an electroplating industry. They observed that optimal pH for fungal isolates was lower (5–5.2) than that for bacterial isolates. Wong and. Fung (1997) reported the removal of nickel from aqueous solution using Cells of *Enterobacter* sp. 4-2 immobilized on magnetites. They observed that the optimal conditions for immobilized cells to remove Ni^{2+} from aqueous solution were buffer at an alkaline pH, the temperature higher than 37°C, and the retention time longer than 30 min. Manuela et al., (2010) investigated removal of nickel from electroplating industry waste water using Brewer's Yeast Strain of Saccharomyces cerevisiae. The maximum removal was attained at pH 6.

2.2.4.6 ADSORPTION

Yu Ji (2010) used activated carbon to remove nickel from aqueous solution. He found that nickel adsorption increased as the pH increases and started decreasing after pH 6. Hasar,(2003) employed adsorption process to remove nickel from aqueous solution using Activated carbon prepared from almond husk by activating without (MAC-I) and with (MAC-II) H_2SO_4 at different temperatures. He found the maximum removal of Ni (II) to be 97.8% at initial concentration of 25mg/l, the adsorbent concentration of 5g/l and optimum pH 5. Kannan and Thambidurai (2008) investigated removal of nickel from aqueous solution by adsorption on to Palmyra palm fruit seed carbon (PPFSC) and commercial activated carbon (CAC). They found that adsorption of nickel (II) was highly pH dependent and the results showed that pH range from 4.0 to 6.0. Demirbas (2002) reported removal of Ni (II) from aqueous solution using activated carbon prepared from hazelnut shell as an adsorbent.

Apart from commercial activated carbons many low cost adsorbents are in use to reduce the operating cost of the process. Chih-Huang, (2002) employed adsorption process to remove Ni (II) onto sludge–ash, a waste produced from a fluidized bed incinerator combusted primarily with biosolids. He found from the results of equilibrium studies that the solution pH was the key factor affecting the adsorption and the adsorption sharply reached a 99% removal at a pH of 8.0 then remained constant over a wide pH region. Periasamy and Namasivayam (1995) used Activated carbon prepared from peanut hulls (PHC), an agricultural waste by-product, for the adsorption of Ni (II) from aqueous solution. They observed the quantitative removal of Ni (II) from 100 mL aqueous solution containing 20 mg/L Ni (II) by 85 mg PHC over a pH range of 4.0 to 10.0. Kumar and. Kirthika (2009) investigated the ability of bael tree (BT) leaf powder to adsorb nickel, Ni^{2+}, from aqueous solutions through batch experiments. From the experiments they found the highest removal rate was 60.21% for Ni^{2+} under optimal conditions and the monolayer adsorption capacity is 1.527 mg Ni per g BT leaf powder.

Garg et al., (2008) employed adsorption process to remove nickel from aqueous solution using an agricultural waste biomass, Sugarcane Bagasse as an adsorbent. They found that the optimum conditions for maximum removal of nickel from an aqueous solution of 50 mg/L were adsorbent dose (1500 mg/L), pH (7.52) and stirring speed (150 rpm). Potgieter 2006 investigated adsorption of nickel from aqueous solution using palygorskite clay as an adsorbent. The adsorption capacity (Q^0) calculated from the Langmuir isotherm was found to be 33.4 mg Ni (II)

g^{-1}. Monier et al., (2010) reported the use of Cross-linked magnetic chitosan-isatin Schiff's base resin (CSIS) to remove nickel from aqueous solution. From the results they observed that the best interpretation for the equilibrium data was given by Langmuir isotherm and the maximum adsorption capacities was 40.15 mg/g.

Onundi et al., (2010) investigated adsorption of nickel from synthesized industrial wastewater using Granular activated carbon produced from palm kernel shell as an adsorbent. The maximum sorption capacity (0.130 mg/g) and removal (55%) were obtained at pH 5, and the equilibrium time was 75 min. Vijayakumaran et al., (2009) testes the efficiency of a carbonaceous adsorbent prepared from an indigenous waste, by acid treatment in the adsorption of nickel from aqueous solution. They observed that the process is pH dependent and the maximum uptake (43mg/g) was obtained at pH 7. The experimental data followed first order reaction equation and showed that the rate is mainly controlled by intraparticle diffusion. Pradhan et al., (2005) employed adsorption of nickel from wastewater onto partially converted crab shell waste, which contains chitosan. They observed the metal uptake by partially converted crab shell waste was successful and rapid within 5 min.

Shyam et al., (2005) reported adsorption of nickel from aqueous solution on to saw dust. They observed that the adsorption of the nickel is dependent on the initial concentrations of adsorbent, sorbate, time of contact and pH. Maximum percent removal of nickel (II) was obtained at pH 9.0 and contact time 1hr. Atul et al., (2011) investigated the use of hydrolyzed poly-methyl methacrylate (HPMMA) as adsorbent in removal of nickel from aqueous solution. They found the optimum conditions for the adsorption to be pH 6; temperature 303 K and adsorbent dose of 5 gL^{-1} was able to remove 59 % of Ni (II) within 60 min of contact time. Vieira et al., (2010) studied adsorption of nickel on calcined Bofe bentonite clay from aqueous solution. They found the maximum adsorption capacity of 1.91mg metal/g of clay at 20°C and pH 5.3.

2.3 COPPER

2.3.1 IMPORTANCE OF COPPER

Copper is a metal of choice for technologists and is an important engineering material having a wide range of industrial applications.

- An important use of copper is in alloys such as brass, bronze, gunmetal, Monel metal and German silver.
- In ceramics and pesticides.
- Used in manufacture of wires for various industries, namely electrical, electronics, automotive, electrical appliances, white goods, etc.
- In copper forming industries (shrivastav, 2009).
- Copper tubing is used in plumbing.
- Computer heat sinks are made out of copper as copper is able to absorb a high amount of heat.
- Copper compounds are widely used as insecticides and fungicides.
- Used in pigments in paints industries.
- Used as mordants (fixatives) in dyeing.
- Used in electroplating.
- Copper is often used to color glass. It is also one component of ceramic glaze.
- Some structures, such as the Statue of Liberty, are made with copper.
- Copper is a great water-proof roofing material. It has been used for this purpose since ancient times.
- Used in refrigerators and air conditioning systems.
- Copper is sometimes combined with nickel to make a corrosion resistant material that is used in shipbuilding.

Apart from industrial use copper plays an important role in all organisms, including man. Copper can be used as a pesticide as well as a nutrient. Copper is an essential nutrient with daily dietary amounts of 1-2 mg requirement for adults. It is a natural anti plaque and anti bacterial agent. It is a component of hemocyanin, the blue, oxygen-carrying blood pigment of lobsters and other large crustaceans. Copper is needed for certain critical enzymes to function in the body.

2.3.2 HARMFUL EFFECTS OF COPPER

Copper is one of the toxic heavy metals, which has been reported to cause neurotoxicity commonly known as “Wilson’s disease” due to deposition of copper in the lenticular nucleus of the brain and kidney failure (Banum, 1982). Moreover, continued inhalation of copper

containing sprays is linked to an increase in lung cancer among exposed workers. Excessive intake of copper causes harmful biochemical effects, and it may cause hemolysis, hepatotoxic and nephro toxic effects in human beings. Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhoea. Copper toxicity leads to serve muscosal irritation, corrosion, widespread capillary damage, hepatic and renal damage and nervous system irritation followed by depression (Krishnamurthy and Vishwanathan, 1991).

2.3.3 SOURCES OF COPPER POLLUTION

Copper enters into the environment through natural and anthropogenic sources. The contamination of air and water, by copper is contributed from the following sources:

- Mining and metalurgy industries.
- Electroplating industries.
- Refining copper ores.
- Milling.
- Petroleum and refining.
- Chloro-alkali industries
- Industrial semlts namely iron and steel, fertilizer industies.
- Explosives.
- Battery manufacturing.
- Copper –ammonium rayon industries and brass industries.

Copper is also discharged into the environment by natural source like windblown dust, volcanic emissions, decaying vegetation, forest fire and sea sprays (Vilar, 2008).

2.3.4 DIFFERENT TECHNIQUES FOR COPPER REMOVAL

According to the WHO standards the maximum contamination level of copper is 1.3 mg L^{-1}. The majority of the industries are discharging effluents containing copper more than its permissible limit. Thus the removal of copper from the industrial wastewater before releasing is necessary. There are several convectional techniques available for the removal of copper ions from wastewaters.

- Chemical precipitation.
- Ion -exchange.
- Membrane filtration.
- Electrochemical methods.
- Biological methods.
- Adsorption methods.

2.3.4.1 CHEMICAL PRECIPITATION

Fu et al., (2007) employed precipitation by 1,3,5-hexahydrotriazinedithiocarbamate to treat waste water containing copper. They conducted experiments at different concentrations 25 mg/L, 50 mg/L, 100 mg/L and found the removal percentage to be 99.0%, 99.3%, and 99.6% respectively at optimum pH 3. Chen et al., (2009) investigated the removal of copper using precipitation process by lime precipitant. The percentage removal achieved was 99.37%- 99.6% at pH 7-11 respectively.

Pauline (2008) reported the removal efficiencies of copper from raw wastewater by chemically enhanced primary treatment (CEPT). The removal was found to be 79%. They found that the Enhanced coagulation and flocculation by ferric chloride and anionic polymer can increase the dissolved metal removal efficiencies. Ngatenah et al., (2010) employed precipitation to remove copper from aqueous solution using Groundwater Treatment Plant Sludge (GWTPS). The optimum conditions to for 100% removal were found to be pH between pH 2 and pH 2.5, contact time varied from 90 min to 480 min.

2.3.4.2 ION-EXCHANGE

Erol and Turkan (2010) investigated the removal of copper from aqueous solution by ion -exchange process using Lewatit CNP 80 resin (weakly acidic) and Lewatit TP 207 (weakly acidic and chelating). They found the optimum pH range for the ion-exchange of copper on Lewatit CNP 80 and Lewatit TP 207 were 7.0–9.0 and 4.5–5.5, respectively. Selvaraj et al., (2007) employed ion-exchange process to treat copper containing waste water by Amberjet 1500H and Ambersep 252H resins. From the adsorption isotherm studies they observed that the

uptake capacity of Cu (II) on 1500H is larger than that of 252H due to the intrinsic ion exchange capacity, while the adsorbate/adsorbate interaction of 1500 is smaller than that of 252H.

Liu and Erhan (2001) used ion-exchange process to remove copper from aqueous solution by Carboxylate-Containing Resin. They determined the cation exchange capacity of the resins to be 3.50 m equiv/g. The maximum adsorption capacity of copper obtained on the resin at pH5.0 was found to be 192 mg/g. Doula (2009) employed clinoptilolite - Fe system to remove Cu, from drinking water. He found that the system has very large metal adsorption capacity and for most of the cases the treated water samples were suitable for human consumption or agricultural use. Dobrevsky et al., (1997) found that purification of galvanic wastewaters containing on the average 55–60 mg Cu (II) dm^{-3}, 140–150 mg SO^{2-}_4 dm^{-3} and of pH about 3.3–3.5 can be successfully carried out by means of ion exchange method.

2.3.4.3 MEMBRANE FILTRATION

Camarilloa et al., (2010) employed ultrafiltration technique by polymer enhanced ultrafiltration ceramic membrane to treat copper from wastewater. They found that the maximum removal achived was 99.5% at optimum pH 5.5. Zhang et al., (2009) reported the use of reverse osmosis process in removal of copper from aqueous solution. The maximum removal were found to be 70% - 95 % for initial metal concentration 20 mg/L-100 mg/L at Low pressure reverse osmosis combined with electrowinning. Molinari et al., (2008) employed PEI as a polymer to study the complexatione-ultrafiltration process in the removal of Cu(II) contained wastewater. From preliminary tests they found that the optimal chemical conditions for Cu(II) complexation by the PEI was pH > 6.0, and polymer/metal weight ratio as 3.0.

Yang and Kocherginsky (2007) investigated the use of hollow fibre supported liquid membrane (HFSLM) system to remove copper from ammonical waste water. Based on the empirical correlations they estimated that the overall mass transfer resistance through HFSLM is higher than total of the element resistances in the tube side, shell side and the membrane. Tanninen et al., (2006) studied removal of copper from waste water using Nanofiltration process at 0.47 M initial metal concentration. They found the maximum removal up to 96%-98% at 20 bar. Hani and Hassan (2004) employed Reverse osmosis and Nanofiltration(NF) technique to remove copper from aqueous solution. From the results they found that high removal efficiency

of the heavy metals could be achieved by RO process (98%). Through NF, up to 90% of the copper ions were removed..

2.3.4.4 ELECTROCHEMICAL TECHNIQUES

Akbal and Camcı (2010)employed Electro-coagulation and Chemical Coagulation to remove copper metal plating wastewater using electrolytic cell using aluminum or iron electrodes and aluminum sulfate or ferric chloride respectively. They observed that chemical coagulation with aluminum sulfate and ferric chloride dosage of 500, and electro-coagulation with iron electrodes at a current density of $10mAcm^{-2}$, electro-coagulation time of 20 min, and pH 3.0 resulted in 99.9% copper removal. Escoba et al., (2006) investigated electro-coagulation process to remove copper from natural waters and simulated wastewater using electrodes of commercial laminate steel. They identified the optimum conditions for the process as pH 7, flow rate 6.3 cm^3/ min and a current density between 31 A/m^2 and 54 $A/m^2$and when the electrode geometric area and time of electrolysis reached critical values, the copper removal reached a maximum value of 80%.

Akbal and Camcı (2010) reported the removal of copper from metal plating industry using Fe- Al electrodes. They found from the results that electrocoagulation with a Fe–Al electrode pair efficiently removed 100% Cu, at an electrocoagulation time of 20min, a current density of $10mA/cm^2$ and at pH 3.0. Khelifa et al., 2005 employed electro coagulation process to treat copper from aqueous solution. The optimum conditions for the maximum Cu removal (99%) was pH 6 and current density 0.3A. Chang et al. (2009a) used electrodeposition process in conjunction with ultrasound to remove copper from wastewater. They found that the technique can successfully remove copper (95.6%) from wastewater.

2.3.4.5 BIOLOGICAL METHODS

Gupta et al., (2006) investigated bisorption of copper aqueous solutions by green alga *Spirogyra* species. They observed the maximum biosorption capacity of 133.3 mg Cu(II)/g of dry weight of biomass at an optimum pH of 5 in 120 min with an algal dose of 20 g/L. Hossain and Anantharaman (2005) employed bisorption of copper by *Thiobacillus ferrooxidans.* They found the maximum biosorption of copper to be 94.25% within 60 hr of inoculation time with optimum pH 4.5 and temperature 40°C for 700ppm initial copper loading. Narsi et al., (2004) used the dead biomass of *spirogyra* species, for the removal of copper from aqueous solution. It was

observed that the *spirogyra* species shown much better sportion in the pH between 6-7 and at contact time of 30 min. The maximum uptake found was 34.94mg/g.

Pairat (2002) employed biosorption of copper using biomass of marine algae as an adsorbent. He found that the sorption capacities were solution pH dependent and the maximum capacity obtained was 0.80 mmol/g at a solution pH 5. The biosorption kinetics was found to be fast; with 90% of adsorption within 15 min and equilibrium reached at 30 min. Muraleedharan and Venkobachar (1990) reported the use of *G. lucidum* as biosorbent to remove copper from aqueous solution.

2.3.4.6 ADSORPTION

Gaikwad (2011) employed adsorption process to remove copper from wastewater using activated carbon derived from coconut shell. From the results he found that the adsorption follows first order kinetics and is slightly endothermic. Zhao et al., (2010) investigated the adsorption of copper onto bentonite embedded in the polyacrylamide (PAAm) gels from aqueous solution. They observed that the sorption increased from about 9% to 97% at pH ranging from 2.4 to 7 and sorption capacity was found to be 33mg/g. Ghassabzadeh et al., (2010) employed adsorption process to remove copper from aqueous solution on to expanded perlite (EP). The optimum conditions for adsorption of copper were found to be pH 6.5 and 240 min contact time. Using the Langmuir model equation, they found the maximum adsorption capacity of EP to be 1.95 mg/g.

Yao et al., (2010) employed batch adsorption studies to remove copper from aqueous solution by chestnut shell. They observed that the adsorption was pH dependent and there was a sharp increase in the copper removal from 20.4% to 92.4% occurred when the pH values of the solutions changed from 2.0 to 5.0. Jaman et al., (2009) used rice husk as a low cost adsorbent for the removal of copper from wastewater. From the experimental results they observed that almost 90–98% of the copper could be removed using treated rice husk. They found the results that the adsorption equilibrium data fitted the Langmuir adsorption model very well at different temperatures. Tariq et al., (2009) employed adsorption of copper from aqueous solution on to pine fruit a solid adsorbent. From the results they found that the adsorption was pH dependent the optimum pH for the removal Cu^{+2} was 7.0, the highest adsorption capacity was found to be 14.1 mg of metal ion per gram of adsorbent at initial concentration of 57.6 mg/L and copper ions.

The percentage removal was found to be 94.1-96% along the whole range of initial concentrations.

Rathnakumar et al., (2009) reported the use of Teak (Tectona grandis L.f) Leaves as an adsorbent to remove copper from aqueous solution. They carried ou experiments at various initial concentrations of Cu (II) (i.e. 0.2 g L^{-1}, 0.4 g L^{-1}, 0.6 g L^{-1}, and 0.9 g L^{-1}), biosorbent dosages (0.3 g L^{-1}, 0.4 g L^{-1}, and 0.5 g L^{-1}), pH (4, 5 and 6) and temperature (20° C, 30°C, and 40°C). From the results they found that the maximum percentage removal was achived at pH 6 and at a temperature of 20°C. Haluk Aydına et al 2008. investigated adsorption of copper from aqueous solution by different adsorbents such as shells of lentil (LS), wheat (WS), and rice (RS). They found the maximum adsorption capacities for Cu (II) on LS, WS and RS adsorbents at 293, 313 and 333K temperature to be 8.977, 9.510, and 9.588; 7.391, 16.077, and 17.422; 1.854, 2.314, and 2.954mg g^{-1}, respectively. Benaïssa and Elouchdi (2007) used dried sunflower leaves as adsorbent to remove copper ions from aqueous solutions. The maximum copper sorption was found to occur at around initial pH 5–6 and the maximum copper uptake was fond to be obtained was qm = 89.37 mg/g (1.41 mmol/g).

Kadirvelu et al.,(2001) reported adsorption of copper from industrial wastewaters onto activated carbon prepared from an agricultural solid waste. They observed that the maximum removal was achieved at pH 4. Yu et al.,(2000) employed adsorption of copper from aqueous solution using saw dust as an adsorbent. They found that adsorption of copper is dependent on its initial concentrations, the amount of sawdust, time of contact and pH of the metal solution. The maximum removal of copper on sawdust was obtained at pH 7.0. The adsorption capacity of sawdust for copper was 1.79 mg/g. Teker and İmamoğlu (1999) investigated adsorption of copper (II) from aqueous solutions,on activated carbon prepared from rice hulls (ACRH). They found that the maximum removal was achived at optimum values of pH, ACRH dosage and contact time were determined to be 5-8, 0.5 g ACRH/25 mL solution an 60 minutes respectively.

Apart from batch studies, adsorption process are also carried out in in different continuous column, which helped in scaling up the laboratory/bench scale data to pilot or industrial scale. The main necessity of an industrial adsorption system is that the adsorbent be

utilized in a fixed or expanded bed with as low a pressure drop as possible. In these process applications, a packed bed column is an effective process for cyclic sorption/desorption, as it makes the most tremendous use of the concentration difference known to be a driving force for heavy metal sorption and results in a improved qualityof the effluent.

Aguayo-Villarreal et al., (2011) employed column adsorption studies for removal of zinc from aqueous solution using chicken feathers an adsorbent. They observed from the results that the characteristics of the breakthrough curves are dependent of the column operating conditions especially pH and feed flow rate. Helen et al., (2010) reported the adsorption behaviour of Ni and Zn from aqueous systems onto activated carbon prepared from *Hevea brasiliensis* sawdust column mode studies under different operating conditions. It was observed from the results that the adsorption capacity increased with increase in the initial metal ion concentration and decreased adsorption capacity with flow rate for both the metals. They also observed that the adsorption capacity comparatively remained constant with bed height which shows that it is independent of bed height.

Pereira et al, 2009 investigated adsorption of zinc from electroplating wastewater using column experiments onto modified wood sawdust and sugarcane begasse. From the results the maximum adsorption capacities Q_{max} were found to be 46 and 60 mg/g, for MB2 and MS2, respectively. The regeneration process of the column proved to be efficient for both adsorbents MS2 and MB2, confirming the ablity of these materials for removing and recuperating Zn^{2+} ions from electroplating wastewater. Doan et al.,(2008) tested adsorption capacity of wheat straw in removal of zinc and nickel using fixed bed column. From the results they found that the amount of metal ions adsorbed and the adsorption rate of both Zn^{+2} and Ni^{+2} generally increased with the liquid pH from 4.0 to 7.0 and when temperature increased from 30 to 35ºC.

Vijayaraghavan et al., (2004) investigated the ability of crab shell to remove nickel (II) ions from aqueous solution using a packed bed up-flow column. They conducted experiments at different bed heights (15–25 cm) and using different flow rates (5–20 ml/min) in order to obtain experimental breakthrough curves. From the results it was found that the elution efficiency was greater than 99.1% in all the seven cycles. Wilson et al., (2001) employed column adsorption studies to remove zinc from contaminated water onto bone charcoal.

2.4 SCOPE OF PRECENT WORK.

The literature review outlines that heavy metal pollution is one of the serious issues in the present scenario. In order to solve this problem there is a need for low-cost process which can be used with ease. One such type of process is adsorption process which is accepted universally as the latest method of treating industrial/mine wastewater for removal of soluble toxic components and is simple and convenient in operating.

Generally many adsorbents have been employed for the removal of heavy metals, which have shown high removal efficiency. But there is a scope for further research to explore new materials which are low cost. In this regard Sponge Iron plant waste (SIP) which is an industrial waste is considered to be one of the low cost materials.

In the present work, an attempt was made to removal of Zinc, Nickel, and Copper from aqueous solution onto HCl treated SIP waste using both batch and column techniques.

The SIP waste was treated with HCl to increase the adsorption capacity. The physical and-chemical properties before and after treatment of the adsorbent were analyzed. The adsorption capacity was studied as a function of contact time, adsorbent dose, pH, initial metal concentration, temperature for all the three metals. Different adsorption isotherm models were employed in order to estimate the optimum adsorption conditions. Different Kinetic models were also studied to now the rate controlling mechanism of the process. Thermodynamic parameters such as standard Gibbs energy (G°), enthalpy (H°), and standard entropy (S°) were calculated for each process using the experimental data. Continuous column experiments were carried at different bed heights and flow rates at optimum pH. The results obtained were well compared with the results reported by other adsorbents in the literature.

3 MATERIALS AND METHODS

3.1 PREPARATION OF ADSORBENT

Sponge iron plant waste form a local sponge iron industry, Mahavir Fero Pvt. Ltd., situated at Kalunga was collected. The collected sample was pulverized to pass through a set of sieves according to the ASTM Method D 2013 and was dried in an oven at 100 ± 5°C for 24 hr. It was then subjected to surface modification process by soaking in HCl, which increases the proportion of active surface (Argun et al., 2007). The oven dried adsorbent was washed several times with distilled water, to remove any particles adhering to the surface. The dried adsorbent was added to 500ml conical flask containing 250 ml of 1N HCl solution. The mixture was left overnight and filtered to remove the sorbent, followed by washing several times with distilled water to make it neutral. The adsorbent is again dried at an oven temperature of 85°C for 2hr.

3.2 CHARACTERIZATION OF ADSORBENT

3.2.1 PHYSICAL PARAMETERS

3.2.1.1 MOISTURE ANALYSIS

The moisture analysis of the SIP waste was studied using standard ASTM Method D 3173. The adsorbent was dried in a hot air oven at 110ºC for 1h. The percentage moisture was then calculated using the following equation:

$$Moisture\ in\ \ analysis\ \ \ sample, \% = \left[(A - B) / A \right] \times 100 \qquad (1)$$

Where: A = grams of sample, and

B = grams of sample after heating.

3.2.1.2 VOLATILE MATTER ANALYSIS

Volatile matter in the SIP waste was determined using ASTM standard Test Method D 3175. The sample was heated for 7 min at 950ºC in preheated muffle furnace. The volatile matter was then calculated the following equations:

$$Weight\ \ loss,\% = \left[(A - B)/A\right] \times 100 \quad (2)$$

Where: A = weight of sample used, g, and

B = weight of sample after heating, g

$$Volatile\ matter\ \ in\ \ analysis\ \ sample,\% = C - D \quad (3)$$

Where: C = weight loss, %, and

D = moisture, %.

3.2.1.3 ASH CONTENT ANALYSIS

Ash content in the SIP waste was determined using ASTM standard Test Method D 3174. The sample was heated in a muffle furnace for 4h at 750˚C. The Ash content was calculated using the following equations:

$$Ash\ \ in\ \ analysis\ \ sample,\% = \left[(A - B)/C\right] \times 100 \quad (4)$$

Where: *A* = weight of capsule, cover, and ash residue, g,

B = weight of empty capsule and cover, g, and

C = weight of analysis sample used, g.

3.2.1.4 IODINE NUMBER

Iodine number of the SIP waste was determined using standard ASTM Test Method D 4067. The sample was added to 100mL of 0.100 *N* iodine solution and shacked vigorously for 30 ±1 s and filtered. The filtrate was then titrated with standardized 0.100 *N* sodium-thiosulfate solution until the solution was a pale yellow. 2 mL of the starch indicator solution was added and titrated with sodium thiosulfate until colorless solution was obtained. Iodine number was calculated by the formula given below.

$$M = [A - (DF)(C)(126.93)(50)] / E \quad (5)$$

Where: M = carbon, g,

$A = (N_2)$ (12693.0),

N_2 = iodine, N

DF = dilution factor

C = residual iodine, and

E = estimated iodine number of the carbon.

3.2.1.5 ANALYSIS OF SPECIFIC SURFACE AREA

The specific surface area of the powder was analyzed by nitrogen adsorption at 77 K in BET surface analyser (Quanta Chrom-USA). Degassing at 200°C for 2 h was performed prior to measurement.

3.2.1.6 ZETA POTENTIAL

The zeta potential of the adsorbent was obtained by analysis in different pH by using an equilibrium method in batch system (Smiciklas et al., 2000). 200mg of adsorbent was added to 20mL sodium chloride 0.1mol/L with pH adjusted among 1 and 12. The samples were stirred for 1h at room temperature (about 25 C), and the final pH was measured.

3.2.2 CHEMICAL PROPERTIES

3.2.2.1 FTIR ANALYSIS

The organic functional groups present in the SIP waste were determined using FTIR analysis. The analysis was carried out using FTIR-3500 spectrophotometer. For measuring the absorption spectra pellets (press disk) were used. The samples were ground along with 200 mg of KBr (spectroscopic grade) in a mortar and pressed into 10 mm diameter disks less than 10 tons of pressure and high vacuum, and 16 scans at a resolution of 4 cm^{-1} measured between 600 - 4000 cm^{-1} were used.

3.2.2.2 SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

The SIP before and after were analysed using SEM/EDX (SEM - JEOL, JSM 6480 LV) at 1000X magnification. From SEM analysis the surface texture is known. EDX gives the elemental analysis.

3.3 CHEMICALS

All the chemicals used were of analytical reagent grade. Zinc metal, nickel chloride, and copper sulphite were used for preparation of stock solutions. Hydrochloric acid and Sodium hydroxide were used to adjust the solution pH. Distilled water was used throughout the experimental studies.

3.4 STOCK SOLUTION PREPARATION

Stock zinc solution (100mg/L) was prepared by dissolving 100 mg zinc dust power in a slight excess of 1+1 HCl and diluted to 1000ml with distilled water. Stock solution of 1000 mg/l Cu (II) ion is prepared dissolving copper sulphate pentahydrate ($CuSO4.5H_2O$) purchased from MERK India Ltd in water. To do this 3.772gm $CuSO4.5H_2O$ is added in distill water contained in 1000ml volumetric. Stock solution of 1000mg/L Ni (II) ion is prepared by dissolving Nickel chloride punched from MERK India Ltd in water. To do this 3.246g $NiCl_2.6H_2O$ is added in distill water contained in 1000ml volumetric

3.5 INSTRUMENTATION

The list of the instruments used during the adsorption experiments and there functions are given in the Table 1

TABLE 3.1: List of Instruments

Instruments	Makers	Function
Analytical Balance	Sartorius	Weight Measurement
pH meter	EuTech Instruments	Measurement of pH
BET apparatus	Quanta Chrom-USA	Surface area of the adsorbent
Ultra-pure water system	Sartorius	Preparation of the stock solution, throughout the experiment etc.
Atomic Absorption spectrophotometer	A Analyst 200, Perkin Elmer	Estimation of metal ion concentration
Shaker	Lab Companion model SI-300R	Batch adsorption studies of heavy metals

FTIR	Perkin Elmer, resolution on $4cm^{-1}$	Analyze the organic functional groups present in the adsorbent
SEM-EDX	SEM - JEOL, JSM 6480 LV.	Surface texture and Elemental analysis of sample

3.6 ADSORPTION EXPERIMENT

Batch adsorption experiments were carried out in a shaker at room temperature using a series of conical flasks containing desired dose of adsorbent in a predetermined concentration of zinc, nickel and copper metal solutions for a fixed duration. Samples were collected at different time interval. The supernatant was separated by filtration and analyzed through AAS to estimate the metal ion concentration. Experiments were carried out at different initial pH values. The initial pH of the solution was adjusted with either HCl or NaOH. The percent removal of metals from the solution was calculated by the following equation.

$$\%removal = \frac{C_0 - C_e}{C_0} \times 100 \quad (6)$$

Where C_0 (mg/L) is the initial metal ion concentration and C_i (mg/L) is the final metal ion concentration in the solution. Isotherm studies were recorded by varying the initial concentration of metal solution from 10 to 100 mg/L. A known amount of adsorbent was then added into the solutions followed by agitating the mixture at 120 rpm till equilibrium. The amount of the metal uptake was calculated by the difference between the equilibrium concentration and the initial concentration. The amount of metal retained in the solid phase q_e (mg/g) was calculated using the relation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (7)$$

Where m is the mass of adsorbent (g), V is the volume of the solution (L), C_0 is the initial concentration of metal (mg L^{-1}), C_e is the equilibrium metal concentration (mg L^{-1}) and q_e is the metal quantity adsorbed at equilibrium (mg/g).

3.7 ADSORPTION ISOTHERMS

Adsorption isotherm helps in determining the properties of the adsorbents. The isotherm curve can be employed to achieve information about the desorption mechanism that is connected with interaction between the adsorbent and adsorbate molecules. Therefore, these curves are used in determining the effectiveness of an industrial adsorbent. The correct description of experimental adsorption isotherm can be understood in terms of some mathematical equations called adsorption isotherm model equations. These equations are derived assuming an ideal physical model for the adsorption system. The model assumptions are generally a result of experimental observations. The performance in a full scale process stream can be estimated using adsorption isotherm. They help to determine, the possibility to attain a required purity level for a given adsorbent. This is important when multiple impurities are present and one or more impurities are weakly adsorbed. The isotherm also allows calculation of uptake (qe) at equilibrium, which has a main impact on the process economy. It can also be used to calculate the relative performance of different types of adsorbents.

Some of the isotherm models in regular use are:

- Langmuir isotherm model.
- Freundlich isotherm model.
- Dubinin-Radushkviech (D-R) isotherm model.
- Temkin isotherm model.

The study of the adsorption equilibrium was carried out for metal concentrations varying from 10 to 100mgL^{-1}.

3.7.1 LANGMUIR ISOTHERM MODEL

The Langmuir adsorption isotherm (Langmuir, I., 1918) was based on the following assumptions:

- Fixed number of adsorption sites: at equilibrium, at any temperature, a fraction of the adsorbent surface sites (θ) is occupied by adsorbed molecules and the rest (1- θ) is free.
- All sorption processes are homogeneous.
- There is only one sorbate.
- One sorbate molecule reacts with only one active site.
- No interaction between the sorbate species.
- A monolayer surface phase is formed.

The equation proposed by Langmuir was generally applicable to chemisorptions with some limitations involving physical adsorption. With one category of adsorption active centre this equation is applicable to the physical or chemical adsorption on solid surface. As long as its restrictions and limitations are clearly known, the Langmuir equation can be used for describing equilibrium conditions for sorption behaviour in different sorbate-sorbent systems or for diverse conditions within any given system. The Langmuir equation is given by:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{8}$$

The linearization of it leads to the following form:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{9}$$

Where C_e, equilibrium metal concentration, q_m and K_L are the Langmuir constants related to maximum adsorption capacity (mg/g), and the relative energy of adsorption (1/mg), respectively. The essential characteristics of Langmuir isotherm model can be explained in terms of a dimensionless constant separation factor, R_L, defined by:

$$R_L = \frac{1}{1 + K_L C_0} \tag{10}$$

The values of R_L indicates the type of Langmuir isotherm to irreversible (R_L=0), favorable (0<R_L<1), linear (R_L=1) or unfavorable (R_L>1).

3.7.2 FREUNDLICH ISOTHERM MODEL

Freundlich equation is derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces. It is based on the assumption that an exponential distribution of adsorption energies exists for each component.

The Freundlich equation is given by (Freundlich and Heller, 1939):

$$q_e = K_F C_e^{\frac{1}{n}} \tag{11}$$

The logarithmic form of equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (12)$$

Where q_e is the amount of metal ion adsorbed per specific amount of adsorbent (mg/g), C_e is equilibrium concentration (mg/L),K_F and n are freundlich equilibrium constants.

3.7.3 DUBININ –RADUSHKEVICH ISOTHERM

The D-R isotherm is more general than the Langmuir isotherm, because it does not assume a homogeneous surface or constant sorption potential. The D-R equation is:

$$q_e = q_m e^{\left(-\beta\left[RT\ln\left(1+\frac{1}{C_e}\right)\right]^2\right)} \qquad (13)$$

The linear form of this model is expressed by (Peric et al., 2004):

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \qquad (14)$$

Where β is a constant related to the adsorption energy, R (8.314 $Jmol^{-1}\ K^{-1}$) is the gas constant, and T *(K)* is the absolute temperature; and $\varepsilon = RT\ ln\ (1 + 1/C_e)$. The constant β ($mol^2\ KJ^{-2}$) reflects the mean free energy E ($KJ\ mol^{-1}$) of sorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship.

$$E = (2\beta)^{-1/2} \qquad (15)$$

This parameter gives information about chemical or physical adsorption. With the magnitude of E, between 8 and 16 $KJ\ mol^{-1}$, the adsorption process follows chemical ion-exchange, while for the values of E< $8KJmol^{-1}$, the adsorption process is of a physical nature.

3.7.4 TEMKIN ISOTHERM

Temkin isotherm includes a factor that clearly takes in account the interactions between adsorbing species- adsorbate. This isotherm assumes that decrease in the heat of adsorption is

linear and the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm is given by the following equation (Temkin and Pyzhev, 1940):

$$q_e = \frac{RT}{b}\ln\left(aC_e\right) \tag{16}$$

Linear form of Temkin isotherm is given by the following equation:

$$q_e = a + b\ln C_e \tag{17}$$

Where q_e is the amount of metal ion adsorbed per specific amount of adsorbent (mg/g), C_e is equilibrium concentration (mg/L), a is equilibrium binding constant (g^{-1}) and b is related to heat of adsorption (J/ mol) which are Temkin constants.

3.8 ADSORPTION KINETICS MODEL

The study of adsorption kinetics in wastewater is important as it afford important insight into the reaction pathways and into the mechanism of the reaction. Further, it is important to predict the time at which the adsorbate is removed from aqueous solution in order to design a proper sorption treatment plant. Any adsorption process is normally controlled by three diffusive transport processes for the adsorbate:

- From bulk solution to the film surrounding the adsorbent.
- From the film to the adsorbent surface
- From the surface to the internal sites followed by binding of the metal ions onto the active sites.

However, in kinetic modeling all these three steps are assembled together and it is believed that the difference between the average solid phase concentration and equilibrium concentration is the driving force for adsorption. Further, it is recognized from the experimental observations that at optimum agitation speed, the external boundaries have no significant effect. Therefore application of the kinetic model depends only on the initial and final concentrations of the solution at different time intervals. It is inaccurate to apply simple kinetic model such as first and second order rate equations to a sorption process with solid surface, which is rarely homogenous. On the other hand, the effects of transport and chemical reaction are often experimentally

inseparable. Numerous kinetic models have been proposed to explain the mechanism of a solute sorption from aqueous solution onto an adsorbent:

- Pseudo first order/Lagergren kinetic model.
- Pseudo second order kinetic model.

3.8.1 PSEUDO-FIRST ORDER MODEL

The Pseudo first order or Lagergen kinetic rate equation for the sorption of liquid-solid system was derived based on solid adsorption capacity. It is one of the most extensively used sorption rate equations for sorption of a solute from a liquid solution. Lagergren equation is given by the following equation (Ho and McKay, 1999a):

$$\frac{dq}{dt} = k_1\left(q_e - q_t\right) \tag{18}$$

Where k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption, q_t (mg/g) denotes the amount of adsorption at time t (min) and q_e (mg/g) is the amount of adsorption at equilibrium.

After definite integration by application of the conditions q_t =0 at t = 0 and q_t = q_t at t = t, Eq. (13) becomes.

$$\log\left(q_e - q_t\right) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{19}$$

The adsorption rate constant, k_1, can be calculated by plotting *log* ($q_e - q_t$) versus t.

3.8.2 PSEUDO-SECOND ORDER MODEL

The pseudo-second-order equation can be written as (McKay and Ho, 1999 b,c):

$$\frac{dq}{dt} = k_2\left(q_e - q_t\right)^2 \tag{20}$$

Integration of Eq. (15) and application of the conditions q_t =*0 at t = 0* and q_t = q_t at t = t, gives

$$\frac{t}{q_t} = \frac{1}{\left(k_2 q_e^2\right)} + \frac{t}{q_e} \tag{21}$$

Where k_2 (g/(mg min)) is the rate constant, k_2 and q_e can be obtained from the intercept and slope.

3.9 ADSORPTION MECHANISM

The adsorption process for porous solid can be divided into three phases i.e. (a) mass transfer (boundary layer/film diffusion), (b) sorption of ions on to sites and (c) intra-particle diffusion. In various cases there is a possibility that intra-particle diffusion will be the rate-limiting step and is given by (Weber et al., 1963).

$$q_t = k_{id} t^{1/2} \tag{22}$$

The plot between q_t vs. $t^{1/2}$ gives the values of coefficient of intra particle diffusion (k_{id}) for adsorption parameter. And the plot between time (t) vs. adsorption percentage at different adsorption parameters may not be linear over the total time range. In that case, more than one step may affect the adsorption process. Therefore the adsorption process can be divided into two different steps, the initial curved portion relates to film diffusion (D_1) and the latter linear portion relates to the diffusion within the adsorbent. If film diffusion is the rate-controlling step, the value of film diffusion co-efficient (D_1) should be in the range 10^{-6} -10^{-8} cm^2s^{-1}. The equation for 'D_1' and 'D_2' are given by (Crank, 1975).

$$\frac{q_t}{q_e} = 6\left(\frac{D_1}{\pi a^2}\right)^{1/2} t^{1/2} \tag{23}$$

$$\ln\left(1-\frac{q_t}{q_e}\right) = \ln\left(\frac{6}{\pi^2}\right) - \left(\frac{D_2 \pi^2 t}{a^2}\right) \tag{24}$$

'D1' can be calculated from the slope of the plot between q_t/q_e vs. $t^{1/2}$ for the initial curved portion. 'D2' can be calculated from the slope of the curve between ln (1- q_t/q_e) vs.'t'.

3.10 THERMODYNAMIC PARAMETERS

Temperature dependence of the adsorption process is related with several thermodynamic parameters. Thermodynamic parameters can be determined using the equilibrium constant *K* *(q_e/c_e)*. The change in Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) associated to the adsorption process was calculated using the following equations (Azouaoua, 2010):

$$\Delta G° = -RT \ln K \tag{25}$$

Where K= Langmuir constant

T = absolute temperature (^{o}K)

R = universal gas constant (8.314 Jmol^{-1} K^{-1})

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{26}$$

ΔH°, ΔS° can be calculated from the slope and intercept of the vant Hoff's plot of *ln K* vs. *1/T* respectively

3.11 FIXED BED ADSORPTION STUDIES

Continuous adsorption studies were conducted using a Perspex fixed bed column of 3cm ID and 40 cm length. An adjustable plunger with a 250µm sieve was attached at the top of the column is place. At the top of the column, an adjustable plunger was attached with a 0.5mm stainless sieve another sieve of 250µm was placed in the bottom of the column to support the packing. A known quantity of SIP waste was filled in the column. The effects of bed height, flow rate were studied. The metal solution was fed to column at a constant flow rate from bottom to top using a peristaltic pump. The samples were collected from the top of the column at various time intervals and were analyzed for Zn and Ni ions using atomic absorption spectrophotometer.

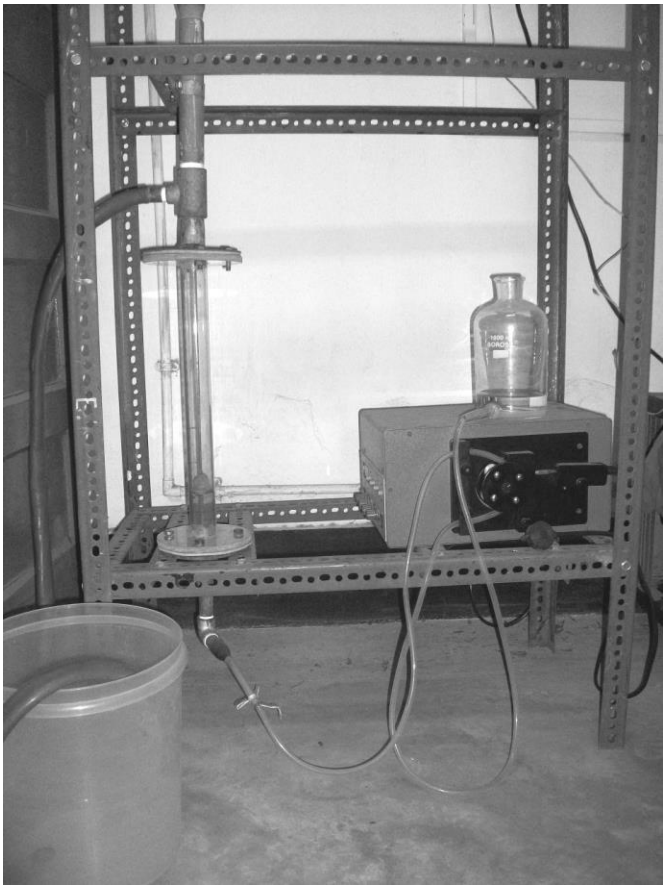

Figure 3.1: Fixed bed column used for the column adsorption studies.

3.12 ANALYSIS OF COLUMN DATA

As the metal solution passes through the column gradually with time the adsorption sites were filled with metal ions and slowly the adsorption zone (where the bulk of adsorption takes place) starts moving up of the column and the effluent concentration start rising with time as the metal solution passes through column. The point at which the concentration of metal in the effluent has suddenly risen to an appreciable value i.e., 1mg/L for the first time is called break point. The time at which the break point is reached is called break through time (t_b) and the portion of the effluent concentration curve as a function of time is called break through curve. The time at which metal concentration in the effluent go beyond 99% of the inlet concentration is called bed exhaustion time (t_e) (Treybal, 1981).

The column adsorption capacity was calculated using the Eq. (27) and is expressed in mg of metal ion adsorbed per gram of adsorbent:

$$Q = \frac{m_{ad}}{M} \tag{27}$$

Where m_{ad} is the quantity of metal ion retained in the column (mg) and M is the mass of the SIP waste (g). m_{ad} is obtained by multiplying the area above the breakthrough curve and the flow rate:

$$m_{ad} = Fa \tag{28}$$

Where F is the flow rate (L h^{-1}) and 'a' is the area above the breakthrough curve (C_t versus t), obtained through numerical integration (Volesky and Prasetyo, 1994).

The total amount of metal ion sent to the column (m_{total}) is calculated from Eq. (29):

$$m_{total} = C_0 F t_e \tag{29}$$

Where C_0 is the initial metal ion concentration (mg L^{-1}) and t_e is the bed exhaustion time (h).

Total metal removal is calculated from Eq. (30):

$$Metal\ \mathrm{Re}moval(\%) = \frac{m_{ad}}{m_{total}} \times 100 \tag{30}$$

The mass transfer zone (Δt) given by Eq. (31)

$$\Delta t = t_e - t_b \tag{31}$$

The critical bed height which is also termed as the height of the mass transfer zone (Z_m) is related to bed height, breakthrough and exhaustion times (Volesky, 2003) and is determined using Eq. (32):

$$Z_m = Z\left(1 - \left(t_e - t_b\right)\right) \tag{32}$$

Effluent volume (V_{eff}) was calculated by using Eq. (33), (Aksu and Gonen, 2003):

$$V_{eff} = Ft_e \tag{33}$$

3.13 MODELING OF BREAKTHROUGH CURVE

The breakthrough curve helps in calculating the performance of a packed bed reactor. The dynamic response of an adsorption column can be determined by the characteristics like time for breakthrough appearance and the shape of the breakthrough curve. The successful design of a column adsorption process requires prediction of the concentration-time profile or breakthrough curve for the effluent. The metal adsorption over different adsorbents is illustrated by many mathematical models. The design of the adsorption process is based on the exact generation of breakthrough curves. The flow rate of the feed solution, concentration of metal ions in the feed, bed height and temperature affect the breakthrough time, exhaustion time and adsorption capacity of the bed. The dynamic behaviour of the fixed bed column was calculated by using Thomas model in the present studied.

3.13.1 THOMAS MODEL

The Thomas model is one of most general and widely used methods in column performance theory. The Thomas model, which assumes Langmuir kinetics of adsorption–desorption and no axial dispersion derived with the adsorption such that the rate driving force obeys second order reversible reaction kinetics. The expression using the Thomas model for adsorption column is given as Eq (34) (Aksu, and. Gonen, 2004).

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{Th} q_0 m}{Q} - \frac{k_{Th} C_0 V_{eff}}{Q} \tag{34}$$

Where 'K_{Th}' is the Thomas rate constant (mL/mg min), 'q_0' is the equilibrium adsorbate uptake (mg/g) and 'm' is the amount of adsorbent in the column.

4 RESULTS AND DISCUSSION- BATCH ADSORPTION

4.1 CHARACTERIZATION OF ADSORBENT

4.1.1 PHYSICAL PROPERTIES

The physical properties of the adsorbent before and after the acid treatment were determined using Eqs: (1), (3), (4), (5) and the values are presented in Table 4.1. The results clearly indicate an increase in the available surface area of the adsorbent.

TABLE 4.1: Characteristics of untreated and HCl treated SIP waste.

Property	Untreated SIP waste	HCl treated SIP waste
Moisture (%)	2.49	2.46
Volatile matter (**%**)	1.9	1.85
Ash content (**%**)	69.9	60.2
Fixed Carbon (%)	25.71	35.49
pH_{PZC}	--	7.2
Iodine no(mg/g)	141	145
BET surface area (m^2/g)	118.5	143.3

4.1.2 CHEMICAL PROPERTIES

4.1.2.1 FTIR ANALYSIS

The FTIR results for both HCl treated and untreated SIP waste were presented in figures 4.1(a) & (b). It was observed that the acid treatment process did not affect the contentedness of functional groups in the adsorbent. The four major peak ranges were almost unchanged before and after the treatment. The peaks in the ranges 1000-1300cm^{-1} and 1600-1750cm^{-1} is attributed to the C-O and C=O of esters and ketones groups respectively. A very broad band near to the 3600cm^{-1} indicates the presence of hydrogen bonded OH group which is due to the adsorption of water on the adsorbent (Azouaoua et al., 2010; Vinke 1994).The peaks near to 2300cm^{-1} are attributed to the presence of nitrile (C≡N) groups to some extent. The presence of C=O shows

very high affinity towards metal adsorption (Chen et al., 2002), that reflects the sorption capacity of the adsorbent.

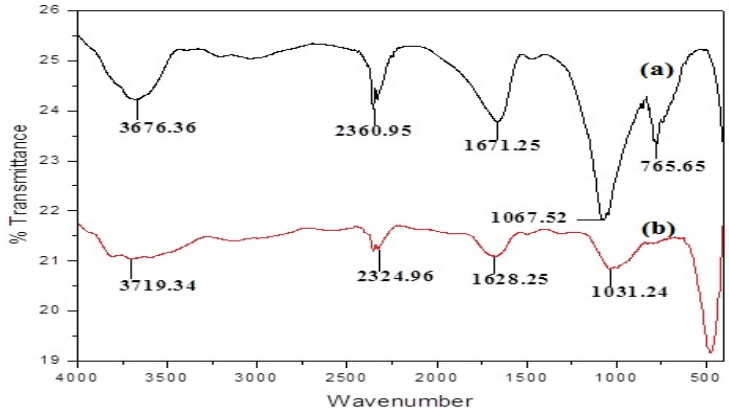

Figure 4.1: FTIR Spectrum of (a) Untreated SIP waste. (b) HCl treated SIP waste.

4.1.2.2 ANALYSIS OF SIP WASTE BY SEM/EDX

Scanning electron microscopic photographs of SIP waste and impregnated SIP waste illustrated the figure 4.2 reveal the structure and indicates that the adsorbents had a porous and homogeneous structure with a deep pore. A progressive change in the surface of the particles had been observed (fig 4.2(a) & 4.2(b).)

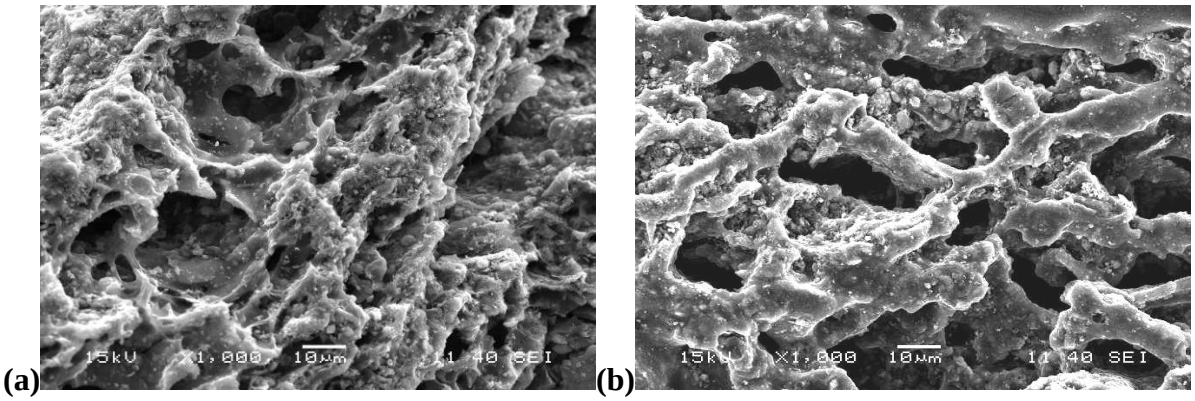

Figure 4.2: SEM analysis of (a) untreated and (b) HCl treated SIP Waste.

The energy dispersive X-ray microanalysis of both the samples was shown in Table 4.2. It indicates the presence of carbon and oxygen in larger percentage with other metals such as Al, Si and Fe etc.

TABLE 4.2: Elemental composition of adsorbents.

Elements	C	O	Al	Si	Fe	S
SIP waste (wt %)	53.06	31.61	2.36	3.67	7.16	0.68
Impregnated SIP waste (wt %)	67.37	19.79	3.31	5.31	1.18	--

4.2 BATCH ADSORPTION STUDIES

4.2.1 ZINC

4.2.1.1 EFFECT OF PARAMETERS

4.2.1.1.1 EFFECT OF CONTACT TIME

Effect of contact time is one of the important parameter in adsorption process. To determine the effect of contact time on adsorption of zinc ions, adsorption experiments were conducting by varying the contact time between the adsorbate and adsorbent in the range of 1–34 min. The concentration of metal ions was 20mg/L, pH was kept as 5.0, and temperature 30°C, while the amount of SIP waste added was 1g/L. From Figure 4.3 the plot depicts that the rate of percent removal of zinc was higher at the beginning. This may be due to the larger surface area of the adsorbent being available at beginning for the adsorption of zinc ions. The HCl treated SIP waste has shown higher percentage removal when compared with Untreated SIP waste. Equilibrium adsorption was reached within a short span of around 26 min indicating that the adsorption sites are well exposed (Orumwense 1996). It is clear for the results that the adsorption of zinc was dependent on contact time. Based on these results, the shacking time was fixed at 26min and HCl treated SIP waste as an adsorbent for rest of the experiments.

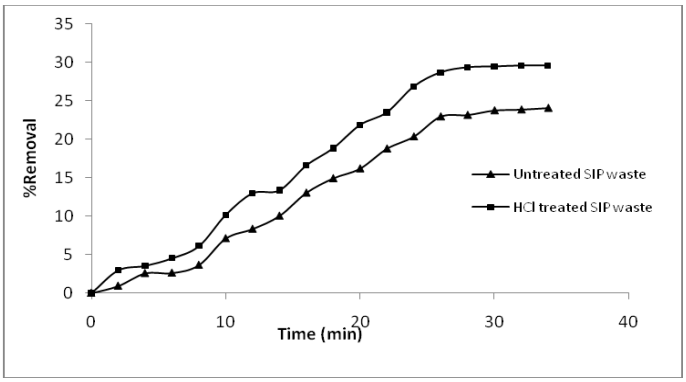

Figure 4.3: Effect of contact time on zinc adsorption using untreated SIP waste,HCl treated SIP waste

4.2.1.1.2 EFFECT OF ADSORBENT DOSE

Effect of SIP waste on Zinc adsorption was studied at 20mg/L, 30°C, and pH 6. The results of adsorbent dose on the percentage removal of Zn metal on SIP waste is reflected in Fig 4.4. Initially the metal uptake increased with adsorbent dose 0.1g/L to 1.5g/L and reached equilibrium at 1g/L. It is due to increased adsorbent surface area and availability of more adsorption sites (Cay et al, 2004). But at 1.5g/L adsorbent dose the metal ions adsorbed per unit weight of adsorbent decreased which is due to the fact that at higher adsorbent dose the solution ion concentration drops to a lower value of q indicating the adsorption sites to remain unsaturated (Amarasinghi and Williams, 2007). Based on these results 1g/L was taken as optimum adsorbent dose for the rest experiments.

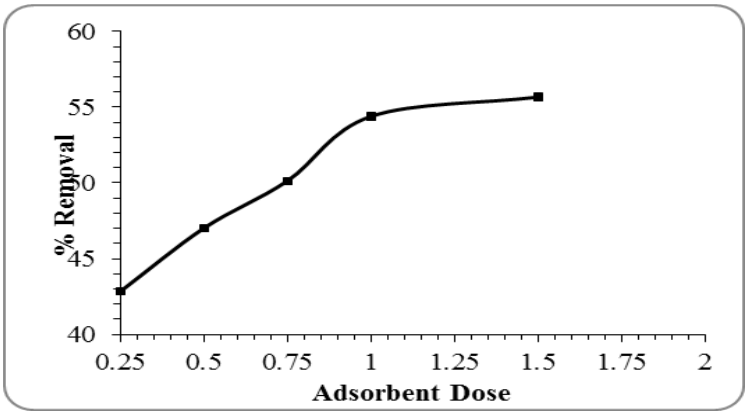

Figure 4.4: Effect of Adsorbent Dose on Zn adsorption.

4.2.1.1.3 EFFECT OF PH

The pH of solution has significant impact on the uptake of metals, since it determines the surface charge of the adsorbent, the degree of ionization and specification of the adsorbent (El-Ashtoukhy et al., 2008). The variation of pH affects the effectiveness as hydrogen ion itself is a tough competing adsorbate. Zinc ions exist in different forms in aqueous solution and the stability of these forms is dependent of the pH of system.

The effect of pH on adsorption of zinc is shown in Fig.4.5. The effect of pH on adsorption of zinc was studied at 30°C, initial metal concentration 20mg/L, adsorbent dose 1g/L by varying the pH of metal solution from 2-7. The percentage adsorption increases with increase in pH. The minimum adsorption was observed at low pH may be due the fact that the presence of higher concentration and higher mobility of H^+ ions favoured adsorption compared to M (II) on the other hand in the acidic medium due to high solubility and ionization of metal ions. The surface of the adsorbent becomes more positively charged at high H^+ concentration such that the attraction between adsorbents and metal cations is reduced. In reverse with increase in pH the negatively charged surface area becomes more thus facilitating grater metal removal. The maximum adsorption was observed within the pH range 4 to 7 which might be due to partial hydrolysis of metal ions (Onundi et al., 2010). Further increase in pH i.e., above 7 of the solution causes precipitation of zinc ions on the surface of the adsorbent by nucleation (Agrawal et al, 2004; Inbaraj and Sulochana, 2006). From these results it was clear that at pH 7 the metal uptake was more i.e., 59.25% based on this pH 7 was taken has optimum pH for rest of the experiments.

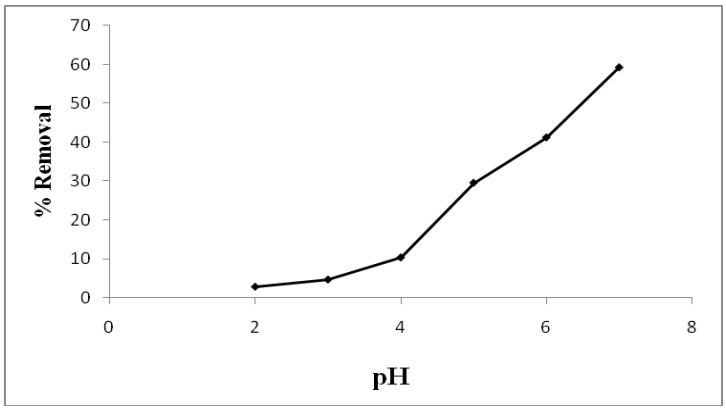

Figure 4.5: Effect of pH on percentage removal of zinc on SIP waste.

4.2.1.1.4 EFFECT OF INITIAL METAL CONCENTRATION

The initial concentration of metal Zinc provides an important driving force to outweigh all mass transfer resistance of metal between the aqueous and solid phases (Wasewar, 2010). Removal of Zinc for various initial concentrations (10 to 100 mg/L) by SIP waste (1g/L) at 26 min contact time and at pH 7 has been depicted in the Fig.4.6. The percentage zinc adsorbed decreased 62.65% to 39.79% with increase in initial concentration from 10mg/L to 100mg/L whereas the

uptake increased from 6.26 - 39.79 mg/g. The saturated specific sites at higher initial metal concentration may be responsible for decreasing percentage removal at increasing initial metal concentration. It reflects that the resistance to mass transfer reduces therefore the removal decreases at higher metal concentration. Similar results were reported by other researchers (Yeddou Mezenner and Bensmaili, 2009; Can and Yildiz 2006).

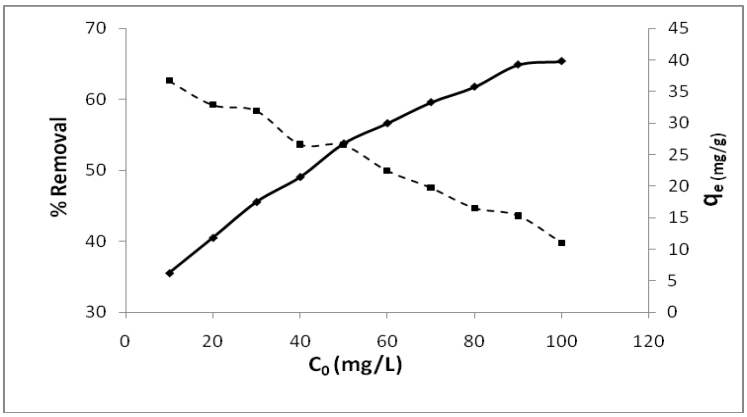

Figure 4.6: Effect of Initial metal concentration on the rate of adsorption.

4.2.1.1.5 EFFECT OF TEMPERATURE

The effect of temperature on the removal of zinc ions by HCl treated adsorbent was studied in the range 25-40°C using 1g/L adsorbent, 30mg/L initial Zinc concentration, and at pH 7. The percentage metal removal decreased from 65.5% to 60.2% with increase in temperature from 25-40°C (fig.4.7). These results indicate that low temperatures are in favour for removal of Zinc ions onto SIP waste. This may be due to a tendency for the Zinc ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. This effect shows that adsorption mechanism related with removal of Zinc onto SIP waste is physical in nature in this situation, in which adsorption take place from the electrostatic interaction, which is in general related with low adsorption heat (Kula et al., 2008). This implies that the adsorption process was exothermic in nature. Similar observation was also reported by (Jiang et al., 2009; Sari et al., 2007).

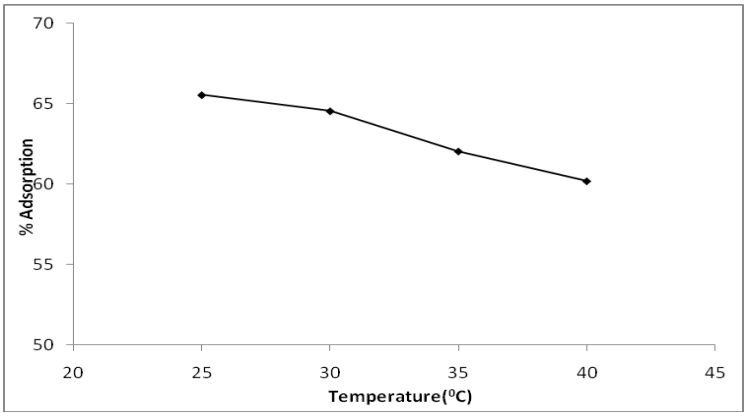

Figure 4.7: Effect of temperature on percentage removal of zinc by SIP waste.

4.2.1.2 ADSORPTION ISOTHERMS

The equilibrium data for the adsorption are commonly known as adsorption isotherms. It is essential to know them so as to compare the effectiveness of different adsorbent materials under different operational conditions and also to design and optimize an adsorption system. Heavy metal adsorption is usually modeled by the classical adsorption isotherms. In this study, four isotherms models were used, Langmuir, Freundlich Dubinin-Radushkviech, Temkin isotherms using Eqs (9),(12),(14),and(16) respectively. The values of various constants of the four models were calculated and were represented in the Table 4.3.

Langmuir, Freundlich Dubinin-Radushkviech, and Temkin adsorption isotherms for zinc from queous solution on SIP waste is presented in Figs 4.8-4.11 respectively. It indicates that the experimental data fitted well to all the isotherm models expect D-R model. By comparing the correlation coefficients, it was observed that Langmuir isotherm gives a good model for the adsorption system, which is based on monolayer sorption on to the surface restraining finite number of identical sorption sites. The maximum adsorption capacity of zinc from Langmuir isotherm was found to be 64.10mg/g and all the R_L values are for 10-100mg/L are 0.92-0.54 which were within the favorable range ($0<R_L<1$). The free energy estimated from D-R model indicates E value as 0.61(KJ/mol) which was less than 8 KJ/mol. It suggests that adsorption process is physical in nature

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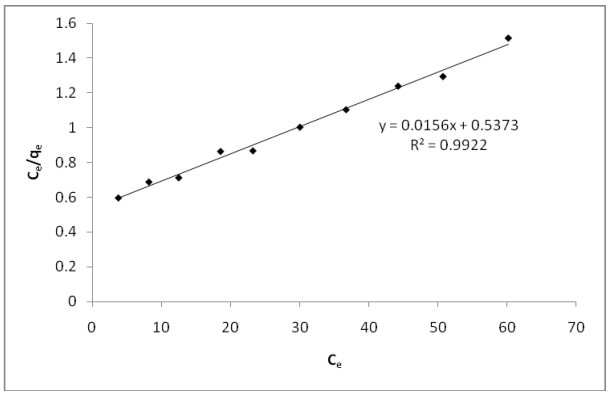

Figure 4.8: Langmuir adsorption isotherm for zinc adsorption

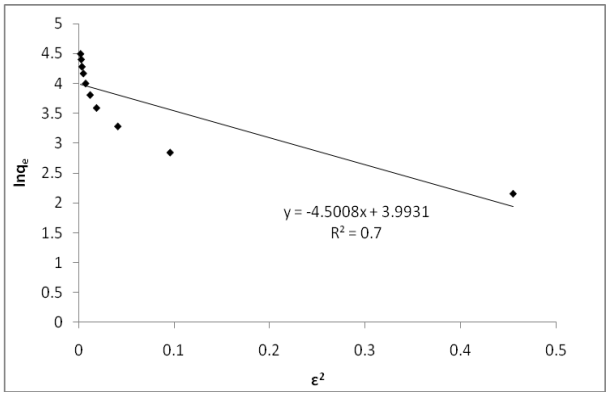

Figure 4.10: D-R isotherm model for zinc adsorption

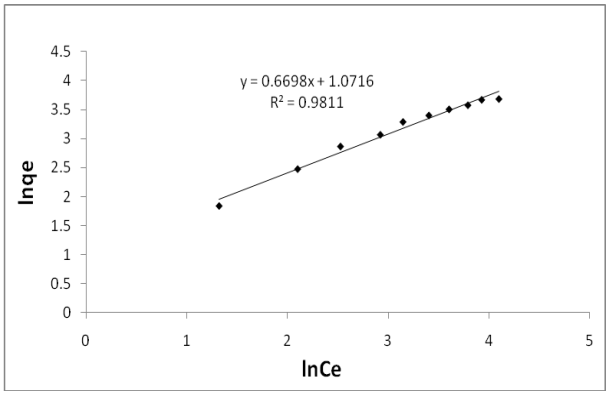

Figure 4.9: Frendluich adsorption isotherm for zinc adsorption

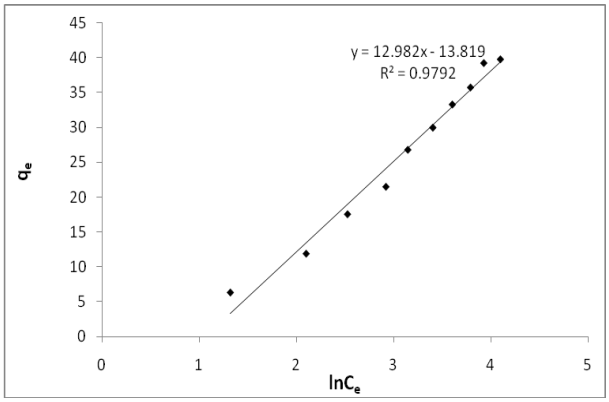

Figure 4.11: Temkin isotherm model for zinc adsorption

TABLE 4.3: Isotherm constants of zinc adsorption

Isotherms	**Values**
Langmuir	
q_m (mg/g)	64.10
K_L(L/mg)	0.029
R^2	0.9922
Freundlich	
K_F(mg/Kg)	2.92
N	1.493
R^2	0.9811
Temkin	
A	1.292
B	194.049
R^2	0.9792
D-R	

$\beta(mol^2kJ^2)$	4.5008
q_m (mg/g)	54.221
R^2	0.700

4.2.1.3 ADSORPTION KINETICS

The kinetics of adsorption was studied for a contact time ranging 1-32 min. The experimental data was fitted to the pseudo first order and pseudo second order kinetic model (fig 4.12 & fig 4.13). The reported R^2 value indicates that the experimental results shows better fit to pseudo-second order model. Hence, the zinc adsorption onto SIP waste seems to be more pseudo-second order. Similar observation was also reported by Azouaou et. al., (2010).

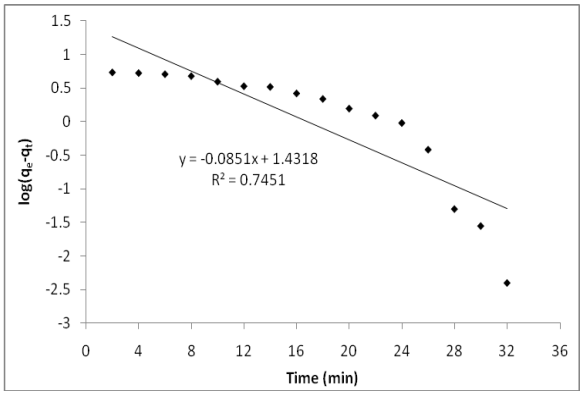

Figure 4.12: Pseudo first order kinetics plot for Zinc Adsorption

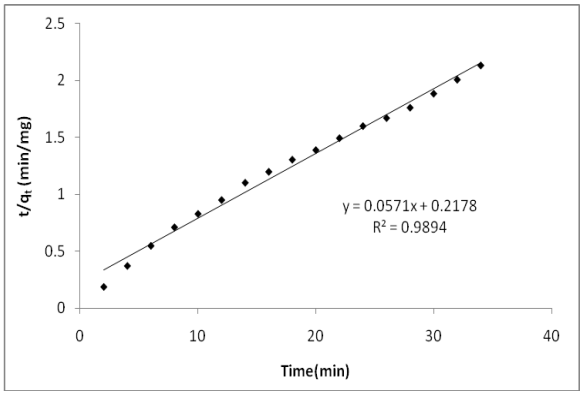

Figure 4.13: Pseudo second order kinetics plot for zinc adsorption

4.2.1.4 ADSORPTION MECHANISM

The contact time variation experiments were used to study the rate-determining step in the adsorption process. Since the particles were agitated at a speed of 180 rpm, it can be assumed that the rate is not controlled by mass transfer from the bulk liquid to the external surface of the particle. As a result, the rate determining step might be either film or intra-particle diffusion. As both act in series, the slower one of the two would be the rate-determining step.

TABLE 4.4: Intraparticle rate parameters, external mass transfer and diffusion coefficients

Diffusion Model	**Values**
Intra Particle Diffusion	
K_{id} (mg/g $min^{0.5}$)	1.472
R^2	0.966
Film Diffusion	

$D_1(m^2/s)$	2.988×10^{-7}
R^2	0.9662
$D_2(m^2/s)$	2.909×10^{-9}
R^2	0.751

The k_{id} values were obtained from the slope of the plot between q_t verses $t^{1/2}$ and the results are shown in Table 4.4. From 'R^2' values, it can be concluded that the process is pore diffusion controlled. The initial curved portion relates to the film diffusion (D_1) and the later linear portion represents the diffusion (D_2) within the adsorbent. Assuming adsorbent particle to be having spherical geometry, the relationship between weight uptake and time using Ficks law is shown equation (23, 24). Using these equations, 'D_1', 'D_2' values were calculated. Table 4.4 shows the 'D_1', and 'D_2' values along with the 'R^2' values. Among the film and pore diffusion film diffusion is considered to be the rate controlling in the adsorption mechanism because of its lower diffusion coefficients.

4.2.1.5 THERMODYNAMIC STUDY OF ADSORPTION PROCESS

The temperature dependence during the adsorption process provides the information about enthalpy and entropy changes associated with the process (Ijagbemi, et al., 2009).The thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy change (ΔH°), and entropy (ΔS°) estimated explains the feasibility and the nature of adsorption process. The results of the thermodynamic calculations are shown in Table 4.5.

The negative value of ΔG° indicates that the process is thermodynamically spontaneous. The negative value of ΔH° for the removal of zinc confirms that the adsorption process was exothermic in nature. The negative value of ΔS° and zinc in bulk phase was in much more chaotic distribution compared to the relatively ordered state of solid phase respectively. Similar results were observed by other researchers Azouaou et.al., (2010). The *lnk* vs *1/T* plot is give in the Fig 4.14

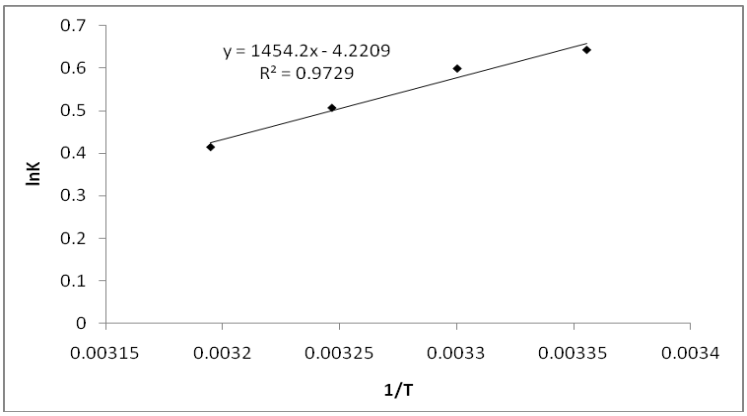

Figure 4.14: The Vant Hoff's plot of *ln K* vs. *1/T*

TABLE 4.5: Thermodynamic parameters of zinc adsorption.

T(K)	ln K	ΔG(KJ mol^{-1})	ΔH(KJ mol^{-1})	ΔS(J mol^{-1} K^{1})
298	3.21	-7.97		
303	3.40	-8.56	-12.09	-35.09
308	3.55	-9.10		
313	3.68	-9.59		

4.2.2 NICKEL

4.2.2.1 EFFECT OF PARAMETERS

4.2.2.1.1 *EFFECT OF CONTACT TIME*

The effect of contact time on nickel adsorption process was determined by conducting adsorption experiments at different contact time between the adsorbate and adsorbent in the range of 1–34 min. The concentration of metal ions was 30mg/L, pH was kept as 6.0, and temperature 30°C, while the amount of SIP waste added was 1g/L. From Fig 4.15, the plot depicts that the rate of percent removal of nickel was higher at the beginning. This may be due to the larger surface area of the adsorbent being available at beginning for the adsorption of nickel ions. Equilibrium adsorption was reached within a short period of around 28 min indicating that the adsorption sites are well exposed (Orumwense , 1996). It is clear for the results that the adsorption of nickel was dependent on contact time. Based on these results, all the batch experiments were conducted with a contact time of 1-30 min.

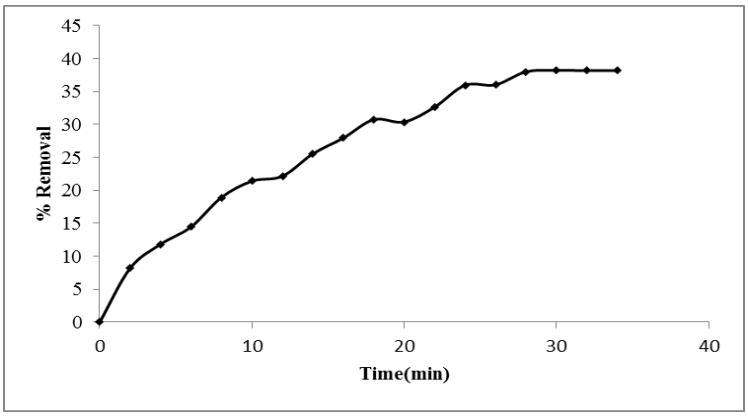

Figure 4.15: Effect of contact time on adsorption of Nickel ions

4.2.2.1.2 EFFECT OF ADSORBENT DOSE:

The effect of SIP waste on Nickel adsorption from aqueous solution was determined by carrying out experiments at initial concentration 20mg/L, temperature 30°C, and pH 6. The results of adsorbent dose on the percentage removal of Nickel metal on SIP waste is reflected in Fig 4.16. Initially the metal uptake increased with adsorbent dose 0.1g/L to 2/L and reached equilibrium at 1g/L. It is due to increased adsorbent surface area and availability of more adsorption sites (Cay et al., 2004). However at 2g/L adsorbent dose the metal ions adsorbed per unit weight of adsorbent decreased which is due to the fact that at higher adsorbent dose the solution ion concentration drops to a lower value of q indicating the adsorption sites to remain unsaturated (Amarasinghi and Williams 2007).Based on these results 1g/L was taken as optimum adsorbent dose for the rest experiments.

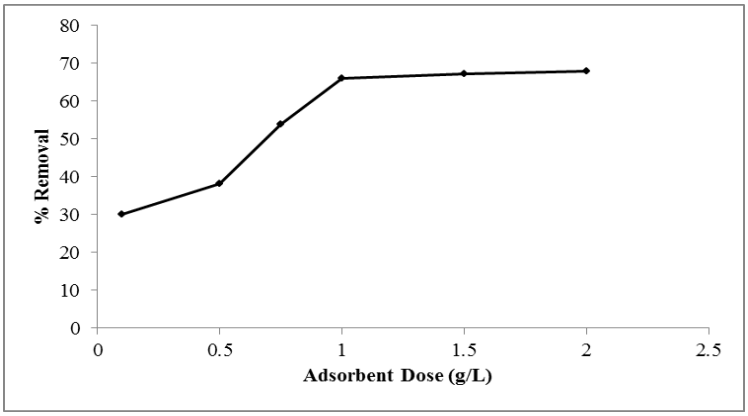

Figure 4.16: Effect of Adsorbent Dose on Zn adsorption.

4.2.2.1.3 *EFFECT OF PH*

The effect of pH is an important parameter in adsorption process, particularly for treatment of wastewater since their initial pH various widely. It is having significant impact on the uptake of metals, as it determines the surface charge of the adsorbent, the degree of ionization and specification of the adsorbent (El-Ashtoukhy et al., 2008). Nickel ions exist in different forms in aqueous solution and the stability of these forms is dependent of the pH of system. The effect of pH on adsorption of nickel is shown in Fig.4.17.

The effect of pH on adsorption of nickel was studied at 30°C, initial metal concentration 30mg/L, adsorbent dose 1g/L by varying the pH of metal solution from 2-6.5. The percentage adsorption increases with increase in pH. The minimum adsorption was observed at low pH may be due the fact that the presence of higher concentration and higher mobility of H^+ ions favoured adsorption compared to M (II) on the other hand in the acidic medium due to high solubility and ionization of metal ions. The surface of the adsorbent becomes more positively charged at high H^+ concentration such that the attraction between adsorbents and metal cations is reduced. In reverse with increase in pH the negatively charged surface area becomes more thus facilitating grater metal removal. The maximum adsorption was observed within the pH range 4 to 6.5 which might be due to partial hydrolysis of metal ions (Onundi et al., 2010).. Further increase in pH i.e., above 6.5 of the solution causes precipitation of Ni ion on the surface of the adsorbent by nucleation (Agrawal et al, 2004, Inbaraj and Sulochana, 2006).From these results it was clear that the maximum metal uptake was at 6.5 pH i.e, 44.38% based on this pH 6.5 was taken has optimum pH for rest of the experiments.

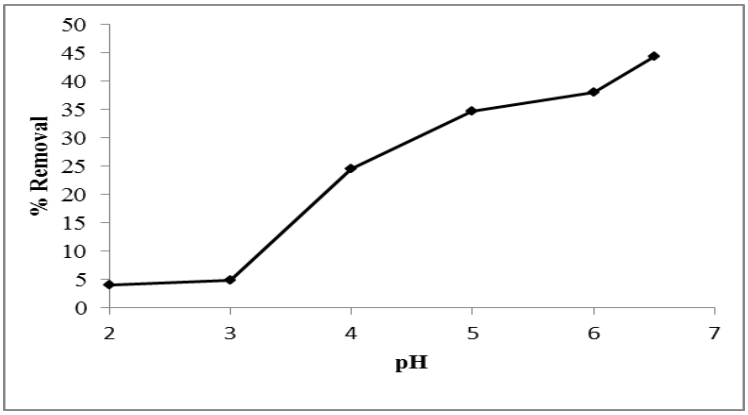

Figure 4.17: Effect of pH on adsorption of Nickel ions

4.2.2.1.4 *EFFECT OF INITIAL METAL CONCENTRATION*

The effect of initial metal concentration on nickel removal was evaluate by conducting experiments by varying initial concentrations from 10 -100 mg/L by keeping adsorbent dose at (1 g/L), pH (6.5), temperature (30°C) and contact time 28 min constant.

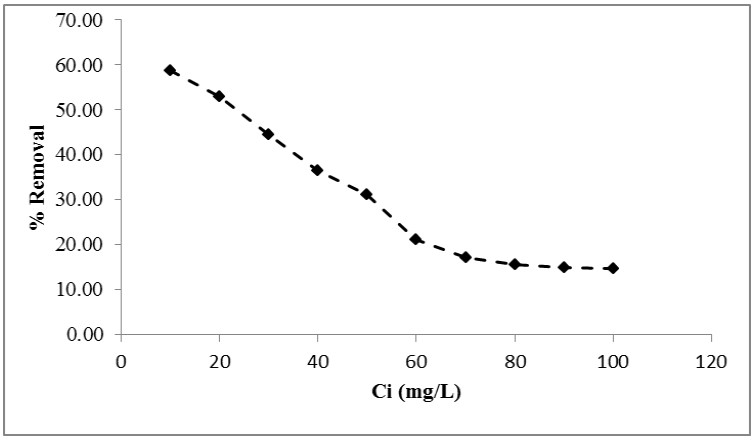

Figure 4.18: Effect of Initial metal concentration on adsorption of Nickel ions

Fig 4.18 depicts the effect of initial metal concentration on percentage removal of nickel. The percentage nickel adsorbed decreased 58.70% to 14.76% with increase in initial concentration from 10mg/L to 100mg/L. The saturated specific sites at higher initial metal concentration are responsible for decreasing metal uptake at increasing initial metal concentration. It reflects that the resistance to mass transfer reduces therefore the uptake decreases at higher metal concentration. Similar results were reported by other researchers (Yeddou Mezenner and Bensmaili, 2009; Can and Yildiz 2006).

4.2.2.1.5 *EFFECT OF TEMPERATURE*

The temperature dependence of the adsorption process is related with several thermodynamic parameters.

The effect of temperature on the removal of nickel ions by HCl treated adsorbent was studied in the range 25-40˚C using 1g/L adsorbent, 30mg/L initial Nickel concentration, and at pH 6.5. The percentage metal removal decreased from 57.4% to 50.7% with increase in temperature from 25-40˚C (fig.4.19). These results indicate that low temperatures are in favour for removal of Nickel ions onto SIP waste. This may be due to a tendency for the Nickel ions to

escape from the solid phase to the bulk phase with an increase in temperature of the solution. This effect shows that adsorption mechanism related with removal of nickel onto SIP waste is physical in nature in this situation, in which adsorption take place from the electrostatic interaction, which is in general related with low adsorption heat (Kula, 2008). This implies that the adsorption process was exothermic in nature. Similar observation was also reported by (Jiang et al., 2009; Sari et al., 2007).

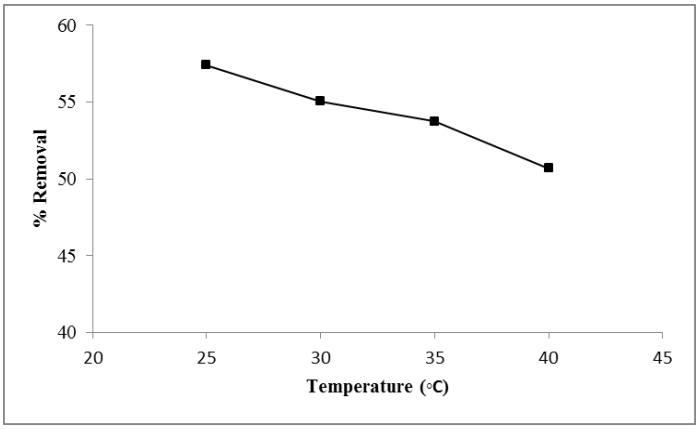

Figure 4.19: Effect of Temperatureon adsorption of Nickel ions

4.2.2.2 ADSORPTION ISOTHERMS

The experimental data obtained was fitted to isotherm models such as, Langmuir, Freundlich Dubinin-Radushkviech, Temkin isotherms using Eqs (9), (12), (14), and (16) respectively. The values of various constants of the four models were calculated and were represented in the Table 4.6.

Adsorption isotherms for nickel adsorption from aqueous solution on SIP waste is presented in Fig 4.20- 4.23. By comparing the correlation coefficients, it was observed that Langmuir isotherm gives a good model for the adsorption system, which is based on monolayer sorption on to the surface restraining finite number of identical sorption sites. The maximum adsorption capacity of nickel from Langmuir isotherm was found to be 14.08 mg/g and the R_L values for 10-100mg/L are 0.2-0.02 which were within the favorable range ($0<R_L<1$). The R^2 value for the Freundlich isotherm was very less which shows that the adsorption of nickel on SIP waste was not a multilayer adsorption. The free energy estimated from D-R model indicates *E* value as 0.4177(KJ/mol) which was less than 8 KJ/mol. It suggests that adsorption process is physical in nature.

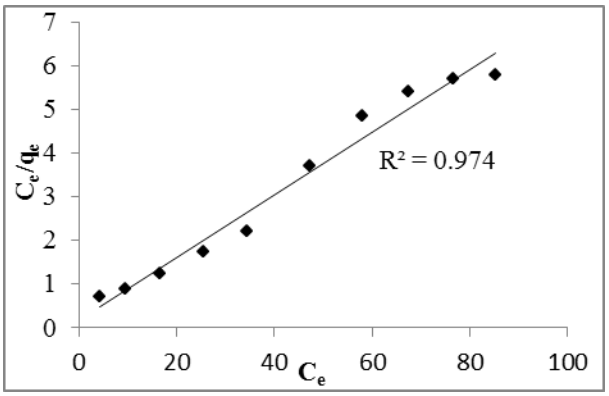

Figure 4.20: Langmuir isotherm model for Nickel adssorption

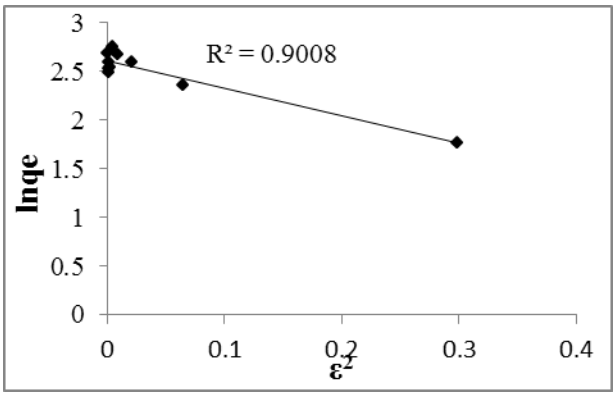

Figure 4.22: D-R isotherm model for Nickel adssorption

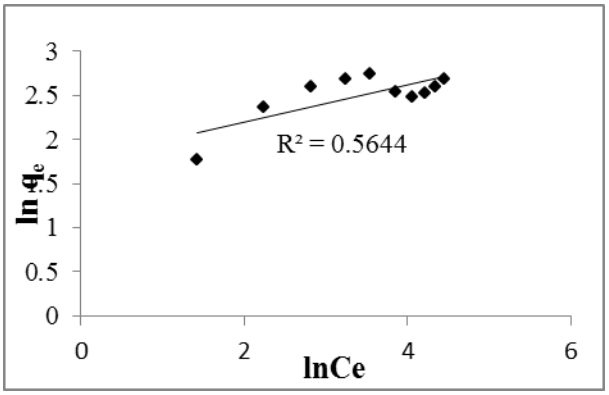

Figure 4.21: Freundlich isotherm model for Nickel adssorption

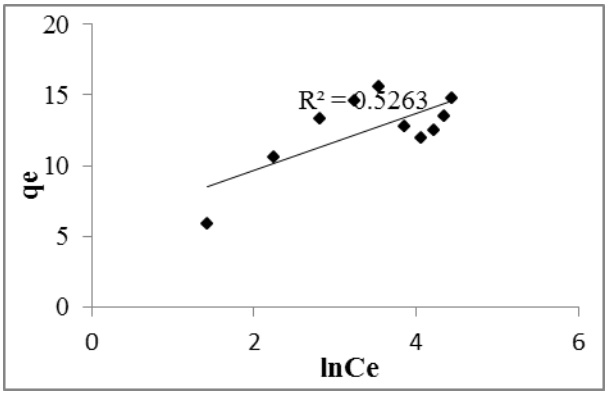

Figure 4.23: Temkin isotherm model for Nickel adssorption

TABLE 4.6: Isotherm constants of nickel adsorption on SIP waste.

Isotherms	**Values**
Langmuir	
q_m (mg/g)	14.08
K_L(L/mg)	0.379
R^2	0.9745
Freundlich	
K_F(mg/Kg)	5.92
N	4.76
R^2	0.564
Temkin	
A	0.989
B	1253.92
R^2	0.526
D-R	
β(mol^2kJ^2)	2.86

q_m (mg/g)	13.68
R^2	0.900

4.2.2.3 ADSORPTION KINETICS:

The kinetics of adsorption was studied for a contact time ranging 1-36 min. The experimental data was fitted to the pseudo first order and pseudo second order kinetic model (fig 4.24 & fig 4.25). The reported R^2 value indicates that the experimental results shows better fit to pseudo-second order model. Hence, the nickel adsorption onto SIP waste seems to be more pseudo-second order. Similar observation was also reported by Azouaou et.al., (2010).

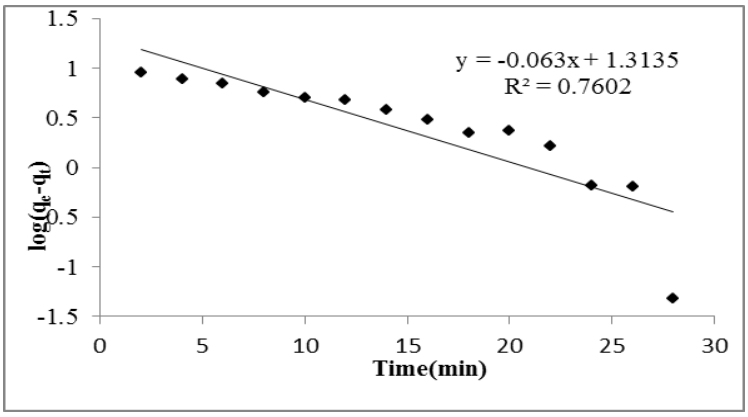

Figure 4.24: Pseudo first order kinetics plot for nickel adsorption.

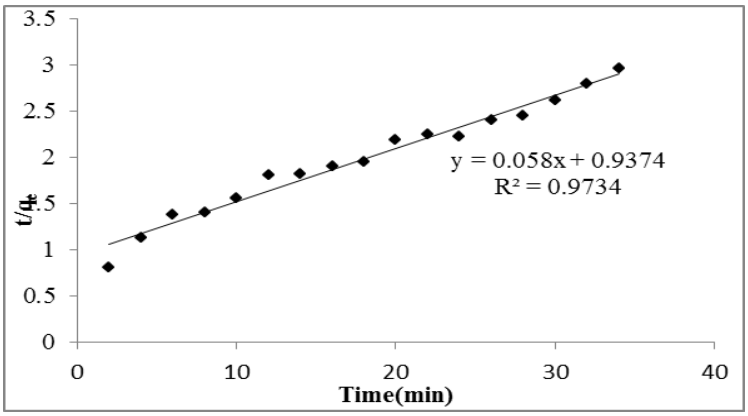

Figure 4.25: Pseudo second order kinetics plot for nickel adsorption.

4.2.2.4 ADSORPTION MECHANISM

The contact time variation experiments were used to study the rate-determining step in the adsorption process. Mass transfer from the bulk liquid to the external surface of the particle was neglected as the particles were agitated at a speed of 180 rpm As a result, the rate determining

step might be either film or intra-particle diffusion. As both act in series, the slower one of the two would be the rate-determining step.

TABLE4.7: Intraparticle rate parameters, external mass transfer and diffusion coefficients

Diffusion Model	**Values**
Intra Particle Diffusion	
K_{id} (mg/g $min^{0.5}$)	2.49
R^2	0.99
Film Diffusion	
$D_1(m^2/s)$	1.91×10^{-7}
R^2	0.994
$D_2(m^2/s)$	2.909×10^{-9}
R^2	0.898

The k_{id} values were obtained from the slope of the plot between q_t verses $t^{1/2}$ and the results are shown in Table 4.7. From 'R^2' values, it can be concluded that the process is pore diffusion controlled. The initial curved portion relates to the film diffusion (D_1) and the later linear portion represents the diffusion (D_2) within the adsorbent. Assuming adsorbent particle to be having spherical geometry, the relationship between weight uptake and time using Ficks law is shown equation (23, 24). Using these equations, 'D_1', 'D_2' values were calculated. Table 4.7 shows the 'D_1', and 'D_2' values along with the 'R^2' values. Among the film and pore diffusion film diffusion is considered to be the rate controlling in the adsorption mechanism because of its lower diffusion coefficients.

4.2.2.5 THERMODYNAMIC STUDY OF ADSORPTION PROCESS

The temperature dependence during the adsorption process provides the information about enthalpy and entropy changes associated with the process (Ijagbemi et al., 2009). The thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy change (ΔH°), and entropy (ΔS°) estimated explains the feasibility and the nature of adsorption process. These parameters were from the slope and intercept of the plot ln$k$ vs. 1/T (Fig 4.26).The results of the thermodynamic parameters calculated using Eq (26) was shown in Table 4.8.

The negative value of ΔG° indicates that the process is thermodynamically spontaneous. The negative value of ΔH° for the removal of nickel confirms that the adsorption process was

exothermic in nature. The negative value of ΔS° and nickel in bulk phase was in much more chaotic distribution compared to the relatively ordered state of solid phase respectively. Similar results were observed by other researchers Azouaou et.al., (2010).

TABLE 4.8: Thermodynamic parameters of nickel adsorption.

T(K)	ln K	ΔG(KJ mol^{-1})	ΔH(KJ mol^{-1})	ΔS(J mol^{-1} K^{1})
298	0.298	-0.738	-13.36	-42.35
303	0.202	-0.510		
308	0.150	-0.384		
313	0.028	-0.072		

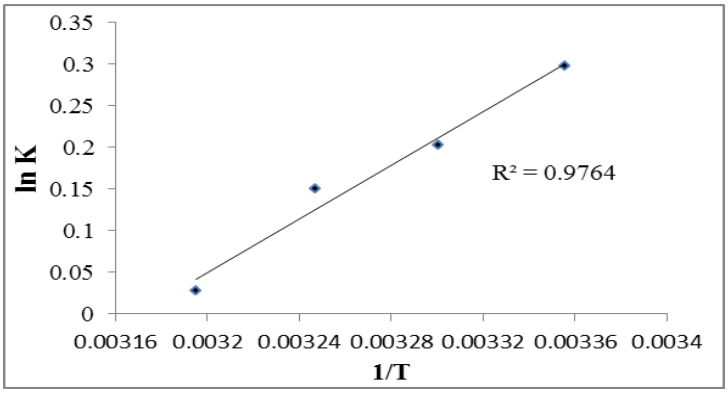

Figure 4.26: Plot of ln*k* vs. 1/T

4.2.3 COPPER

4.2.3.1 EFFECT OF PARAMETERS

4.2.3.1.1 *EFFECT OF CONTACT TIME*

The removal of copper on SIP waste from aqueous solution was studied as function of contact time in the range of 2-34 min at 20mg/L initial metal concentration, 5 pH, 1g/L SIP waste, and 30ºC temperature. The effect of contact time on removal of copper is shown in the Fig 4.27. From the figure it was observed that the rate of zinc removal was higher at the beginning until 30min and, thereafter, the adsorption rate become practically constant. The difference in the degree of adsorption may be due to the fact that in the beginning all the sites on the surface of the adsorbent were vacant and the solute concentration gradient was relatively high (Yeddou

Mezenner and Bensmaili, 2009). As a result, the extent of copper removal decreased with increase in contact time, which is dependent on the number of vacant sites on the surface of SIP waste. Based on these results 30min was considered as the optimum time for the rest of the experiments.

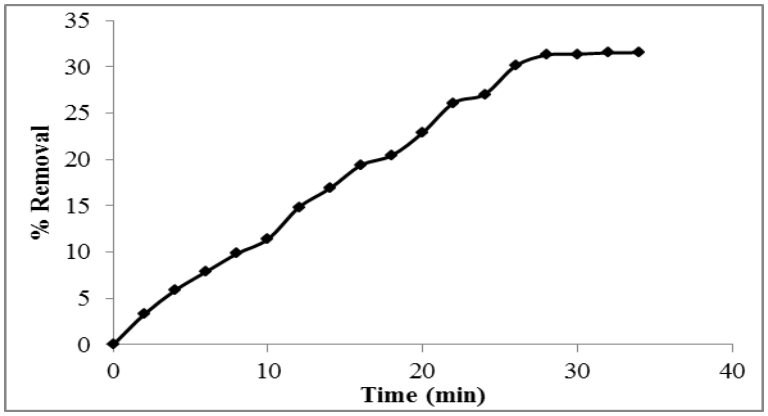

Figure 4.27: Effect of contact time on copper removal.

4.2.3.1.2 *EFFECT OF PH*

The effect of pH on removal of copper using SIP waste was studied by conducting a set of experiments by adjusting the pH from 2-6. The results obtained were shown in the Fig 4.28. As the pH varied from 2-6 the adsorption rate of copper was increased from 5.65-32.75%. The minimum adsorption was observed at low pH may be due the fact that the presence of higher concentration and higher mobility of H^+ ions favoured adsorption compared to M (II) on the other hand in the acidic medium due to high solubility and ionization of metal ions. The surface of the adsorbent becomes more positively charged at high H^+ concentration such that the attraction between adsorbents and metal cations is reduced. Further increase in pH i.e., above 7 of the solution causes precipitation of zinc ions on the surface of the adsorbent by nucleation (Agrawal et al, 2004; Inbaraj and Sulochana, 2006). According to these results pH 6 was taken as optimal value for the rest of the experiments.

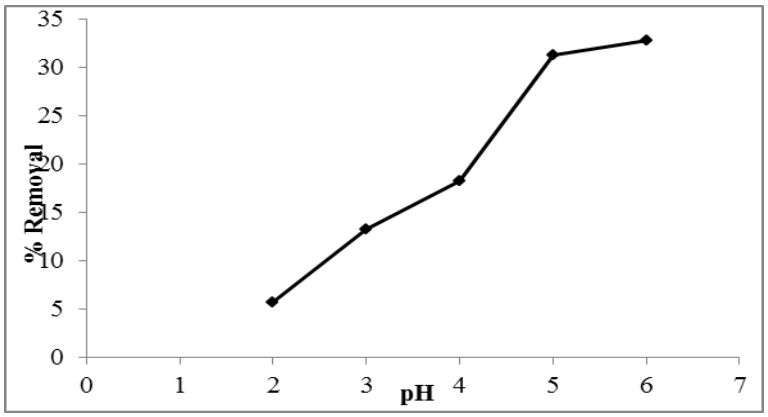

Figure 4.28: Effect of pH on copper removal.

4.2.3.1.3 *EFFECT OF INITIAL METAL CONCENTRATION*

The effect of initial copper concentration on the copper adsorption rate was studied in the rage (10-100mg/L) at pH 6, temperature 30ºC, and 30min contact time. The results presented in the Fig 4.29. From the figure it was observed that the percentage of removal decreased with increasing in initial copper concentration. The poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of moles of copper to the vacant sites available. For a given adsorbent dose the total number of adsorbent sites available was fixed thus adsorbing almost the equal amount of adsorbate, which resulting in a decrease in the removal of adsorbate, consequent to an increase in initial copper concentration. Therefore it was evident from the results that copper adsorption was dependent on the initial metal concentration. Similar results were also reported by other researchers (Nasir et al., 2007; Dahiya et al., 2008).

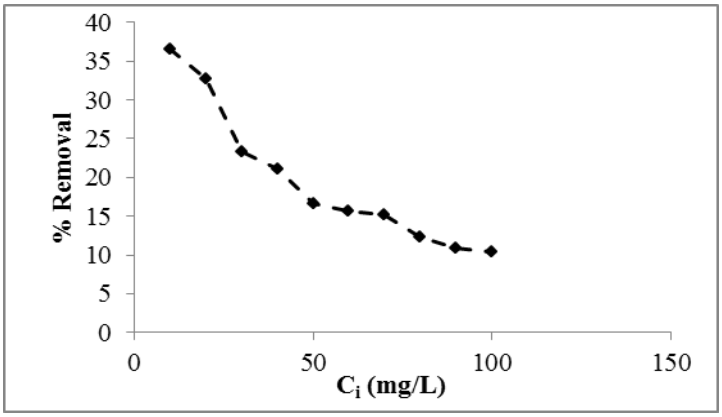

Figure 4.29: Effect of the initial metal concentration on copper adsorption.

4.2.3.1.4 *EFFECT OF TEMPERATURE*

The effect of temperature on the removal of copper ions by HCl treated adsorbent was studied in the range 25-40˚C using 1g/L adsorbent, 20mg/L initial copper concentration, and at pH 6. The percentage metal removal decreased from 37.15% to 33.8% with increase in temperature from 25-40˚C (fig.4.30). The decrease in adsorption percentage with increase in temperature indicated that low temperature was in favour of copper removal onto SIP waste. This may be due to a tendency for the copper ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. This implies that the adsorption process was exothermic in nature. Similar observation was also reported by (jiang et al 2009, Sari et al, 2007).

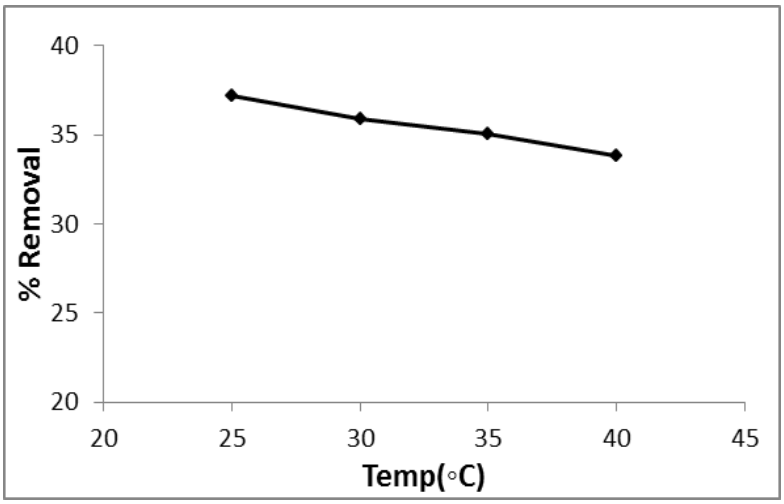

Figure 4.30: Effect of temperature on copper removal by SIP waste

4.2.3.2 ADSORPTION ISOTHERMS

The experimental data obtained from copper adsorption experiments were fitted to different isotherm models such as, Langmuir, Freundlich Dubinin-Radushkviech, Temkin isotherms using Eqs (9), (12), (14), and (16) respectively. The isotherm models were presented in the Figs 4.31-4.34 respectively. The values of various constants obtained from these plots for the four models were calculated and represented in the Table 4.9.

TABLE 4.9: Isotherm constants of copper adsorption.

Isotherms	**Values**
Langmuir	
q_m (mg/g)	11.79

K_L(L/mg)	0.091
R^2	0.987
Freundlich	
K_F(mg/Kg)	2.49
N	2.94
R^2	0.913
Temkin	
A	1.00
B	1063.3
R^2	0.938
D-R	
β(mol^2kJ^2)	16.13
q_m (mg/g)	50.39
R^2	0.709

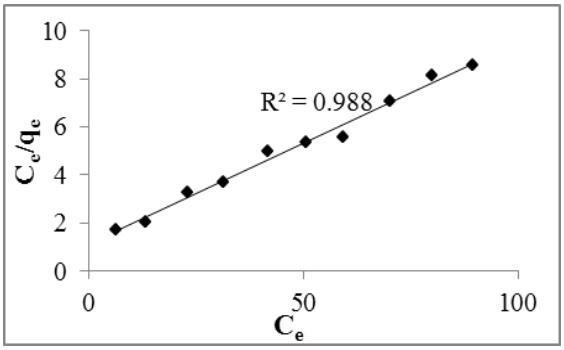

Figure 4.31: Langmuir isotherm model for copper removal.

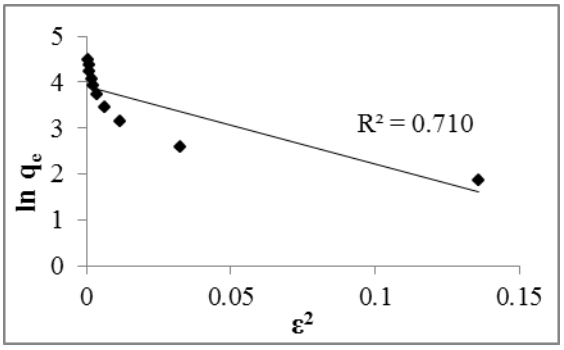

Figure 4.33: D-R isotherm model for copper adsorption.

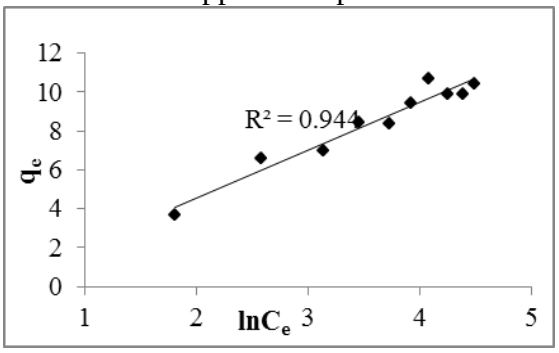

Figure 4.34: Temkin isotherm molel for copper adsorption.

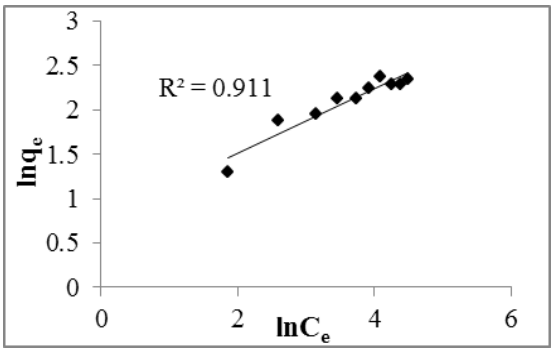

Figure 4.32: Freundlich isotherm model for copper adsorption.

By comparing the R^2 it was observed that the Langmuir isotherm was good fit among the four isotherms. Thus from these results it was apparent that the adsorption of copper onto SIP waste was monolayer sorption. The maximum adsorption capacity of copper from Langmuir isotherm was found to be 11.79mg/g and all the R_L values are for 10-100mg/L are 0.52-0.09 which were within the favourable range ($0<R_L<1$). The free energy estimated from D-R model indicates E value as 0.17(KJ/mol) which was less than 8 KJ/mol. It suggests that adsorption process is physical in nature.

4.2.3.3 ADSORPTION KINETICS

The kinetics of adsorption was studied for a contact time ranging 1-30 min. The experimental data was fitted to the pseudo first order and pseudo second order kinetic model (fig 4.35 & fig 4.36).

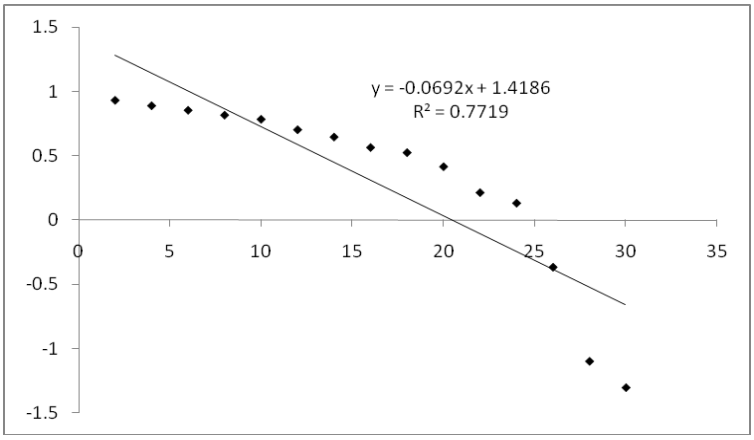

Figure 4.35: Pseudo first order kinetics plot for copper Adsorption

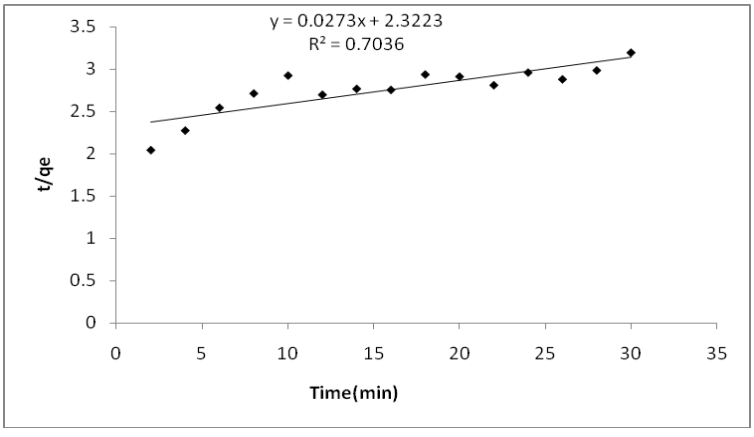

Figure 4.36: Pseudo second order kinetics plot for copper adsorption

4.2.3.4 ADSORPTION MECHANISM

The k_{id} values were obtained from the slope of the plot between q_t verses $t^{1/2}$ and the results are shown in Table 4.10. From 'R^2' values, it can be concluded that the process is pore diffusion controlled. The initial curved portion relates to the film diffusion (D_1) and the later linear portion represents the diffusion (D_2) within the adsorbent. Assuming adsorbent particle to be having spherical geometry, the relationship between weight uptake and time using Ficks law is shown by equation (23, 24). Using these equations, 'D_1', 'D_2' values were calculated. Table 4.10 shows the 'D_1', and 'D_2' values along with the 'R^2' values. Among the film and pore diffusion film diffusion is considered to be the rate controlling in the adsorption mechanism because of its lower diffusion coefficients.

TABLE 4.10: Intraparticle rate parameters, external mass transfer and diffusion coefficients

Diffusion Model	Values
Intra Particle Diffusion	
K_{id} (mg/g $min^{0.5}$)	0.443
R^2	0.979
Film Diffusion	
$D_1(m^2/s)$	2.77×10^{-07}
R^2	0.978
$D_2(m^2/s)$	6.67×10^{-06}
R^2	0.782

4.2.3.5 THERMODYNAMIC STUDY OF ADSORPTION PROCESS

The temperature dependence during the adsorption process provides the information about enthalpy and entropy changes associated with the process (Ijagbemi et al., 2009). The thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy change (ΔH°), and entropy (ΔS°) estimated explain the feasibility and the nature of adsorption process. These parameters were from the slope and intercept of the plot ln*k* vs. 1/T (Fig 4.37).The results of the thermodynamic parameters calculated using Eq (26) was shown in Table 4.11

The negative value of ΔG° indicates that the process is thermodynamically spontaneous. The negative value of ΔH° for the removal of nickel confirms that the adsorption process was exothermic in nature. The negative value of ΔS° and nickel in bulk phase was in much more chaotic distribution compared to the relatively ordered state of solid phase respectively. Similar results were observed by other researchers Azouaou et.al., (2010).

TABLE 4.11: Thermodynamic parameters of nickel adsorption.

T(K)	ln K	ΔG(KJ mol^{-1})	ΔH(KJ mol^{-1})	ΔS(J mol^{-1} K^{1})
298	-0.52	-1.30	-7.38	-29.16
303	-0.57	-1.46		
308	-0.61	-1.57		
313	-0.67	-1.74		

z

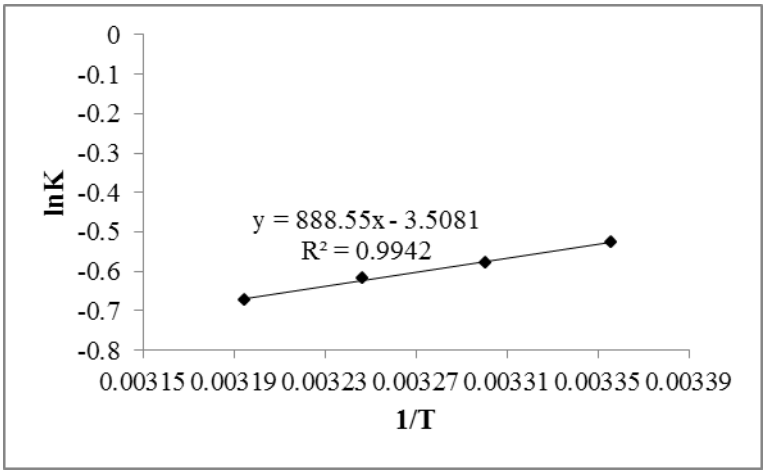

Figure 4.37: Plot ln*k* vs. *1/T*

TABLE 4.12: Comparison of adsorption capacities with other adsorbents at standard conditions.

Metal	Adsorbent	% Adsorption	Work done by
Zn	Modified Groundnut shells	9.57mgg^{-1}	Shukla and Pai (2005b)
	Cocunut shell	99.74%,	Olayinka et al., (2007)
	waste tea	90.74%	Olayinka et al., (2007)
	SIP waste	64.10mgg $^{-1}$,65.5%	present study
Ni	sludge–ash	99%	Chih-Huang, (2002)
	palm kernel shell	0.130 mgg^{-1}	Onundi et al., (2010)
	hydrolyzed poly-methyl methacrylate	59%	Atul et al., (2011)
	SIP waste	14.08 mgg^{-1} ,44.38%	present study
Cu	polyacrylamide	33mgg^{-1}.	Zhao et al., (2010)
	expanded perlite (EP	1.95 mgg^{-1}.	Ghassabzadeh et al., (2010)
	sawdust	1.79 mgg^{-1}.	Yu et al.,(2000)
	SIP waste	11.79mgg^{-1}	present study

4.2.4 CO- ADSORPTION OF ZINC AND NICKEL

Generally Industrial wastewater contains more than one type of metal ions. Therefore, the effect of co-adsorption of multiple metal ions on adsorption of individual ions was estimated. The percentage removal of zinc and nickel from a bimetal solution containing both zinc and nickel at different metal concentrations and temperatures were investigated.

4.2.4.1 EFFECT OF PARAMETERS

4.2.4.1.1 EFFECT OF INITIAL METAL CONCENTRATION

The effect of initial metal concentration on adsorption was investigated by using a wide range of initial metal ion concentrations (10-100mg/L) of the binary solution (Zn, Ni) at pH 6.5,1g/L adsorbent, 30ºC temperature, at 28 min contact time for Zn and 30 min for Ni has been depicted in the Fig.4.38. The percentage removal of zinc and nickel ions decreases from 59.06% to 36.43% and 48.02% to 12.68% respectively with increase in metal concentration from 10-100mg/L. The saturated specific sites at higher initial metal concentration are responsible for decreasing metal uptake at increasing initial metal concentration. It reflects that the resistance to mass transfer reduces therefore the uptake decreases at higher metal concentration. Similar results were reported by other researchers (Yeddou Mezenner and Bensmaili, 2009; Can and

Yildiz 2006).The percentage removal of zinc is more compared to nickel has in the case of non-competitive adsorption conditions. The difference in adsorption behavior of zinc compared to nickel may be due to the different affinity of metal ions for the different donor atoms (i.e. oxygen, sulphur and nitrogen) in the SIP waste structure. This behavior may also due to the complexing groups present on the adsorbent resulting in a relatively high adsorption of zinc ions. Similar results were reported by other researchers (SolmazKarabulut et al., 2000).

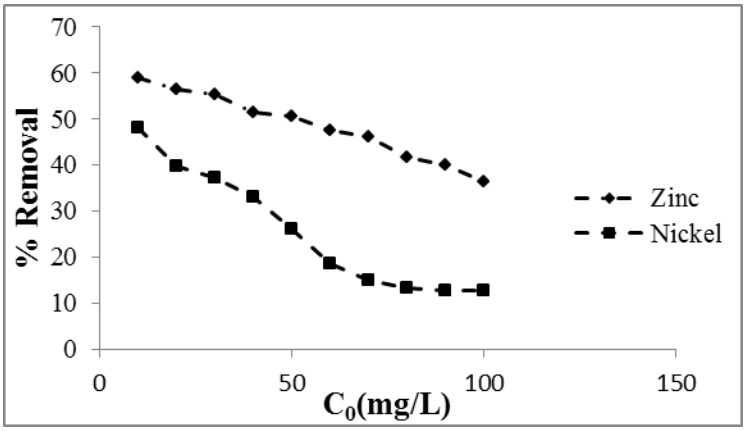

Figure 4.38: Effect of initial metal concentration on adsorption of Zn, Ni ions onto SIP waste.

4.2.4.1.2 EFFECT OF TEMPERATURE

Effect of temperature on co- adsorption of Zn and Ni onto SIP waste was examined within a range of 25-40ºC at pH 6.5, 1g/L adsorbent dose, 20mg/l of initial metal concentration. The percentage zinc removal decreased from 62.85% to 57.29% and nickel removal decreased from 48.02-42.03% with increase in temperature from 25-40˚C (fig.4.39).

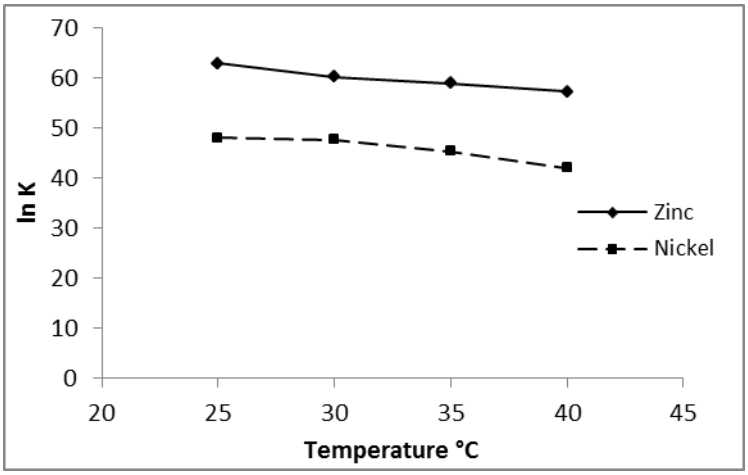

Figure 4.39: Effect of temperature on Co-adsorption of Zn and Ni ions onto SIP waste.

The decrease in adsorption percentage with increase in temperature indicated that low temperature was in favor of Zn, Ni removal onto SIP waste. This may be due to a tendency for the copper ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. Thus it implies that the adsorption process was exothermic in nature. This has shown similar trend as in the single metal removal.

4.2.4.2 EFFECT OF CO-ADSORPTION

The percentage removal of zinc and nickel from a bimetal solution containing both zinc and nickel at the solution pH of 6.5, the liquid temperature of 25ºC was investigated. The percentage removal of zinc and nickel for both individual ion and bimetal solution has been depicted in Fig 4.40. The figure shows that the removal of zinc was higher than that of nickel for both individual ion adsorption and co-adsorption with the bimetal solution. There was no significant effect on the adsorption zinc due to the presence of nickel. In contrast, the removal of nickel decreased from 57.40% for the single-ion nickel solution to 48% in the presence of zinc co-adsorption. In the mass transfer standpoint, the diffusivity of zinc ($7.016\times10^{-10}m^2\ s^{-1}$) was about 15% higher than that of nickel ($6.132\times10^{-10}m^2\ s^{-1}$) (Anderko, and Lenka, 1998). Therefore, the mass transfer rate of zinc from the bulk liquid to the surface of the adsorbent was higher than that of nickel; hence, the adsorption of zinc was better. Similar results were reported by other researchers (Doan et al., 2008).

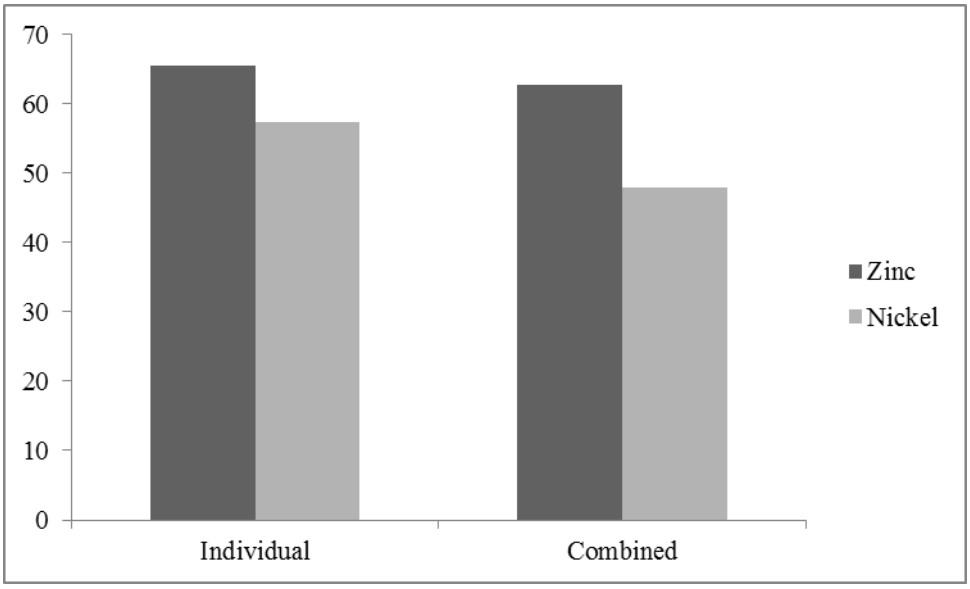

Figure 4.40: Effect of co-adsorption on the adsorption of individual metal ions on SIP waste**.**

5 RESULTS AND DISCUSSION- COLUMN ADSORPTION

5.1 EFFECT OF PARAMETERS

5.1.1 EFFECT OF BED HEIGHT

The effect of bed height was investigated by conducting experiments at constant feed concentration of 20mgL^{-1}, flow rate 20mLmin^{-1}, temperature 25ºC, and pH 6.5 based on the batch adsorption experiments with bed height ranging from 5 to 15cm. Figs 5.1& 5.2 shows the effect of bed height on adsorption of zinc and nickel. The different operating parameters for zinc and nickel are given in Tables 5.1 and 5.2 respectively. From the results it was observed that both breakthrough time and exhaustion time increased with increase in bed height, as more binding sites are available for sorption, it also resulted in a broadened mass transfer zone. As the bed height increases, the length of the bed through which the solution containing metal ion passes also increases. The percentage adsorption increased from 40% – 62.05% for zinc and 31.23%- 56.43% for nickel with increase in bed height form 5 to 15cm for both the metals and this is due to the increase in SIP waste dosage in larger beds which provide increased surface area and more binding sites for adsorption (Fu and Viraraghavan 2003).

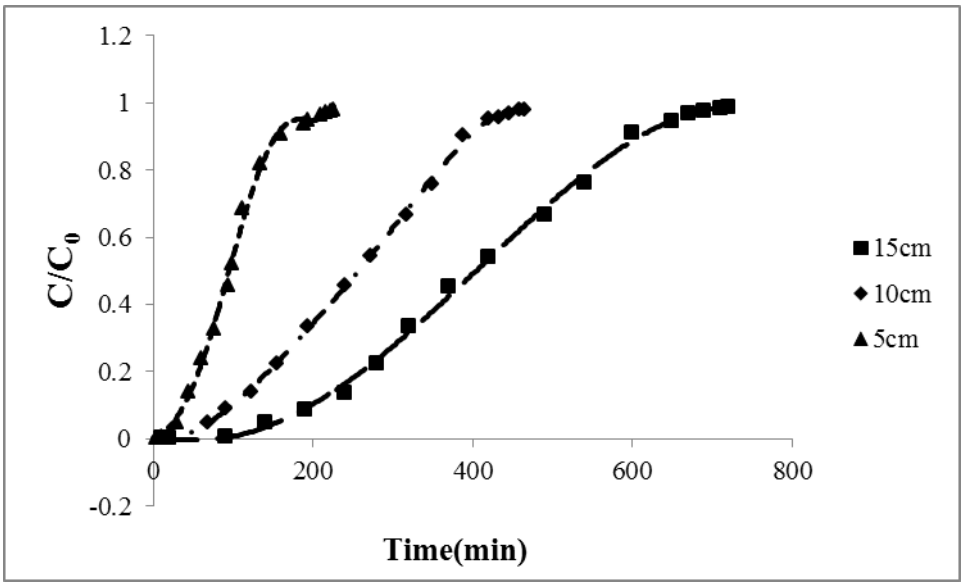

Figure 5.1: Break through curve for zinc at different bed heights.

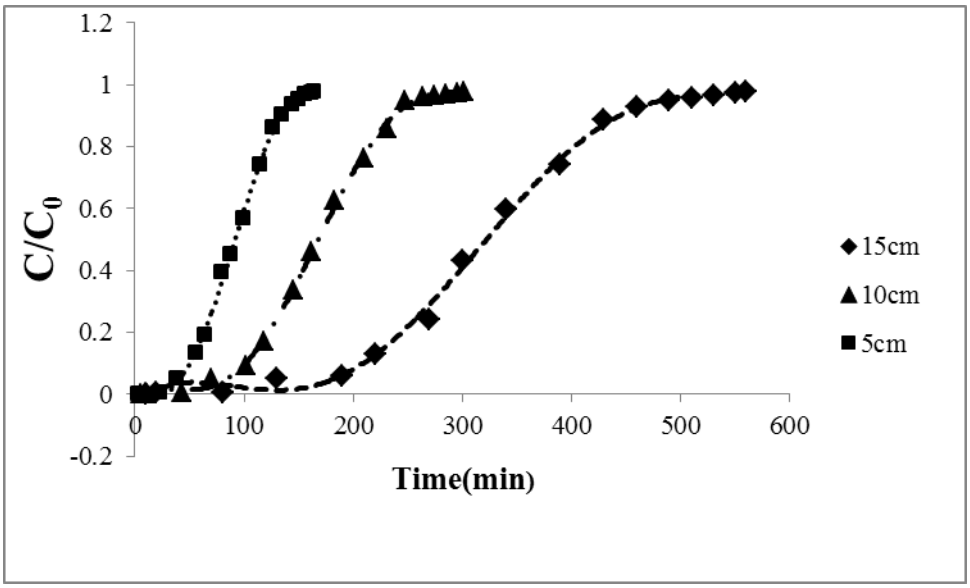

Figure 5.2: Break through curve for nickel at different bed heights

5.1.2 EFFECT OF FLOW RATE

The influence of flow rate on the adsorption of Ni and Zn by SIP waste was investigated by keeping initial metal ion concentration (20mgL^{-1}), temperature (25ºC) and bed height (5cm), and pH 6.5 constant and varying the flow rate from 10 to 20mLmin^{-1}. At low flow rate the column performance was well. Initially the adsorption was very rapid at lower flow rates may be associated with the availability of adsorption sites to capture metal ions around or inside the adsorbent. In the next stage of the process due to the gradual occupancy of these sites, the uptake becomes less effective. From the Figs. 5.3 and 5.4, an earlier breakthrough and exhaustion time was observed which resulted in steeper breakthrough curves, when the flow rate was increased from 10 to 20mLmin^{-1}. The flow rate also strongly influenced the metal uptake capacity. When flow rate increased from 10 to 20mLmin^{-1} the % removal decreases from 60.75 to 40.92% for zinc and 56.17 to 31.23% for nickel. Results are shown in Tables 5.1 and 5.2. The credible reason behind this is that when the residence time of the metal in the column is not long enough for adsorption equilibrium to be reached at that flow rate, the metal solution leaves the column before equilibrium occurs. Consequently, the contact time of metal ions with the adsorbent is very short at higher flow rate, causing a reduction in removal efficiency (Ghorai and Pant, 2005).

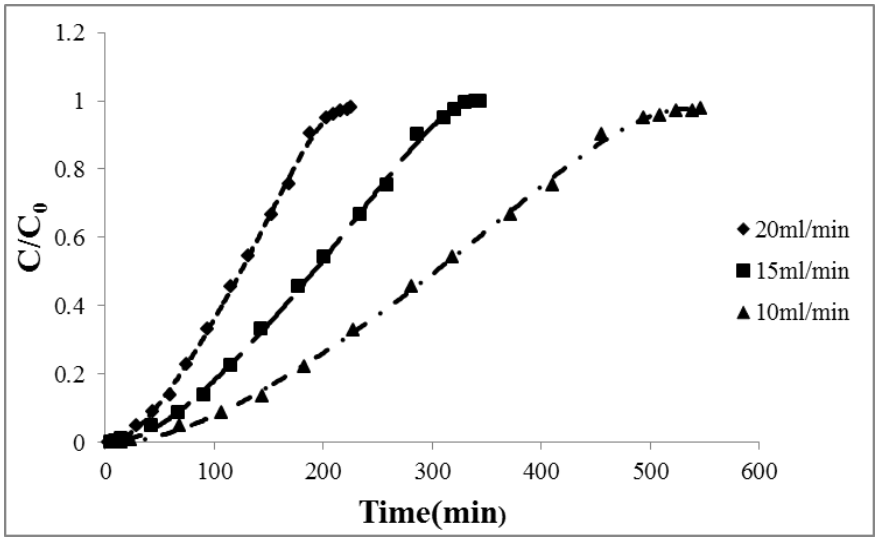

Figure 5.3: Break through curves for zinc at different flow rate.

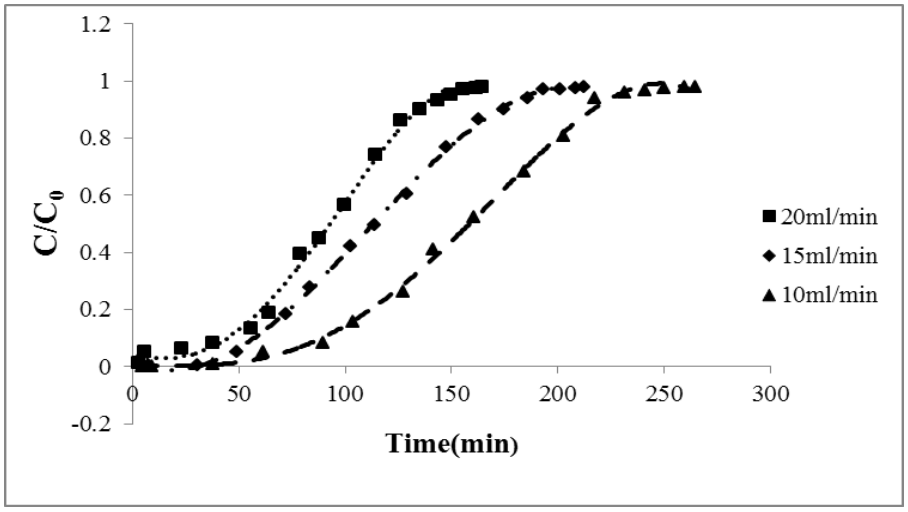

Figure 5.4: Break through curves for nickel at different flow rate.

TABLE 5.1: Zinc adsorption data on SIP waste in a fixed bed column at different operating conditions.

Z (cm)	F(ml.min^{-1})	Q exp(mg.g^{-1})	t_b(min)	t_e(min)	$\Delta t=(t_e-t_b)$	$Z_m=Z(1-(t_b-t_e))$	% Removal
5	20	26.13	28	209	181	910	40.92
10	20	26.52	68	432	364	3650	60.78
15	20	25.36	140	650	510	7665	62.05

5	15	30.82	43	320	277	1390	48.94
5	10	36.26	68	523	455	2280	60.75

TABLE 5.2: Nickel adsorption data on SIP waste in a fixed bed column at different operating conditions.

Z (cm)	F(ml.min^{-1})	Q exp(mg.g^{-1})	t_b(min)	t_e(min)	$\Delta t=(t_e-t_b)$	$Z_m=Z(1-(t_b-t_e))$	% Removal
5	20	22.84	38	149	111	560	31.23
10	20	21.87	69	274	205	2060	51.49
15	20	22.36	130	530	400	6015	56.43
5	15	25.76	61	193	132	665	50.12
5	10	34.75	50	250	200	1005	56.17

5.2 REGENERATION STUDIES

The reusability of adsorbent is related to the application potential of adsorption technology. Thus, regeneration of the adsorbent material is of critical importance in the economic development. Regeneration is the removal of metal adsorbed on the SIP waste using an eluting agent. This must produce small volume of metal concentrates suitable for metal-recovery process, without damaging the capacity of the adsorbent, making it reusable in several adsorptions and desorption cycles. Regeneration should also guarantee that eluted solution is not posing any disposal problem waste in terms of high acidity. In the present study, elution of zinc and nickel were carried out using HCl as desorbing agent at constant flow rate of 20mLmin^{-1}, and bed height of 5cm preloaded with 20mgL^{-1} of zinc and nickel as feed concentration shown in the Fig 5.5and 5.6. After the recovery of metal ion, the regenerated SIP waste was thoroughly washed with distilled water and again loaded with zinc and nickel solution of concentration of 20mgL^{-1}. The column regeneration studies were carried out for adsorption–desorption cycles for both zinc and nickel. The same operating conditions were employed for all the adsorption–desorption cycles. The actual bed length remained constant during the regeneration cycles. A decreased breakthrough time was observed as the regeneration cycles progressed. This behaviour is mainly due to stable deterioration of SIP waste because of continuous usage. The regeneration efficiency was found to be 62.51% and 82.29% for zinc and nickel respectively.

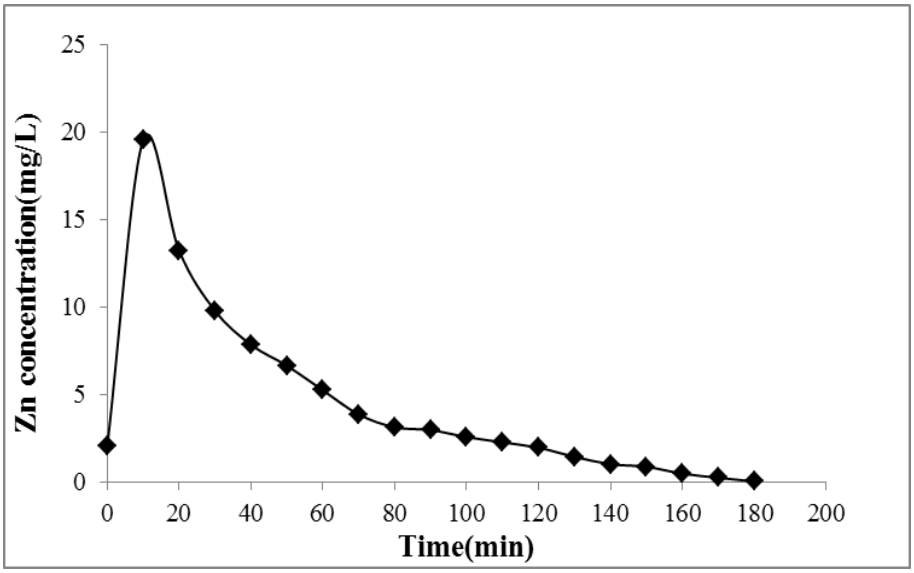

Figure 5.5: Elution curves for zinc columns using 0.1 N HCl.

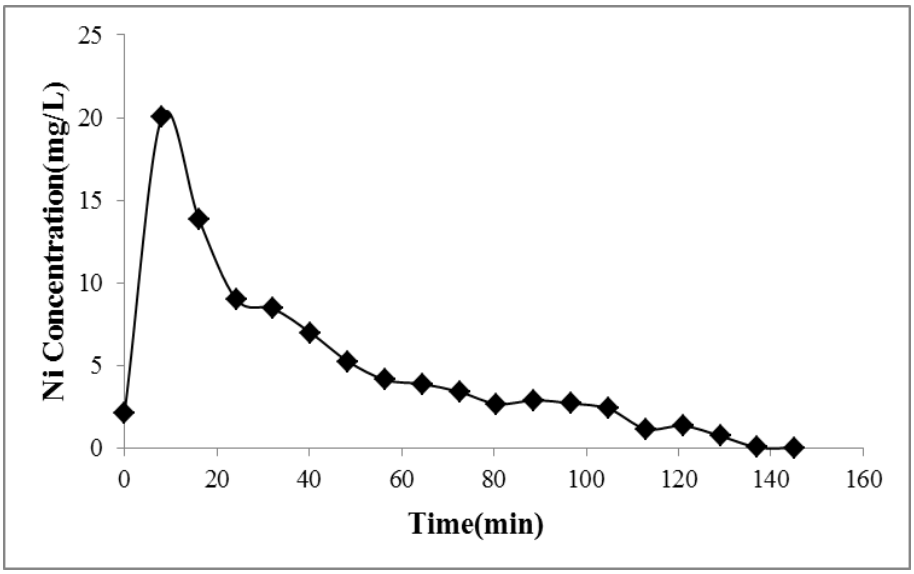

Figure 5.6: Elution curves for nickel columns using 0.1 N HCl

5.3 MODELING OF BREAKTHROUGH CURVE

5.3.1 THOMAS MODEL

Thomas model was used to predict the breakthrough curves under varying experimental conditions. The values of the thomas model parameters were given in the Table 5.3. From the results it was observed that Qo values calculated from the Thomas model is close to the Q, exp

values obtained experimentally for both zinc and nickel. Therefore model gave good agreement between experimental and calculated breakthrough curves.

TABLE 5.3: Thomas Model constants for zinc and nickel

Metal	Z (cm)	F(ml.min^{-1})	Q exp(mg.g^{-1})	Parameters of Thomas Model		
				K_{Th}(L.min^{-1}.mg^{-1})	Q_0(mg.g^{-1})	R^2
Zn	5	20	26.13	0.000685	30.01	0.9777
	10	20	26.52	0.000965	28.19	0.9615
	15	20	25.36	0.002015	25.94	0.9238
	5	15	30.82	0.00157	29.28	0.9067
	5	10	36.26	0.00082	35.15	0.9517
Ni	5	20	22.84	0.000915	24.27	0.9893
	10	20	21.87	0.00178	19.22	0.9762
	15	20	22.36	0.00312	22.15	0.98
	5	15	25.76	0.00233	27.59	0.9768
	5	10	34.75	0.00192	35.33	0.9913

6 CONCLUSION

The present study on adsorption of Zinc, Nickel and Copper from aqueous solutions using SIP waste suggested the following conclusions:

- SIP Waste showed very minor changes in surface properties after HCl treatment.
- Influence of process parameters such as pH, adsorbent dosage, temperature, contact time, initial metal concentration was moderate such that they can affect the removal efficiencies of the heavy metals.
- The adsorption process was dependent on metal solution pH. The optimum pH for Zn, Cu and Ni were 7, 6 and 6.5 respectively.
- Effect of temperature showed that adsorption decreased with increase in temperature and the optimum was found to be 25◦C.
- The optimum amount of adsorbent dosage was found to be 1 mg/L.
- Initial metal concentration showed negative impact on the adsorption efficiency i.e at lower levels the adsorption was higher.
- The adsorption data was fitted to different adsorption isotherm model equation that indicated Langmuir model to fit best for all three metals i.e. Zn, Ni, and Cu with R^2 values 0.992, 0.974, 0.987 respectively.
- Kinetics studies of adsorptions for all three metals revealed that the adsorption process follows a pseudo second order for all of them.
- Among the film and pore diffusion models, film diffusion is considered to be the rate controlling in the adsorption mechanism because of its lower diffusion coefficients

- The thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy change (ΔH°), and entropy (ΔS°) estimated explained that the adsorption of Zn, Ni, and Cu on SIP waste is exothermic in nature.

- Co-adsorption studies showed that the removal of zinc was higher than that of nickel for both individual ion adsorption and co-adsorption. There was no significant effect on the adsorption of zinc in presence of nickel.

- Colum studies revealed that when bed height increased from 5cm to 15cm, the percentage adsorption increased from 40% – 62.05% for zinc and 31.23%- 56.43% for nickel Also when flow rate increased from 10 to 20mLmin^{-1} the % removal decreases from 60.75 to 40.92% for zinc and 56.17 to 31.23% for nickel.

- The elution of zinc and nickel were carried out using 0.1N HCl as desorbing agent at constant flow rate of 20mLmin^{-1}, and bed height of 5cm preloaded with 20mgL^{-1} of zinc and nickel as feed concentration. The regeneration efficiency was found to be 62.51% and 82.29% for zinc and nickel respectively.

- The Thomas model used to predict the breakthrough curves under varying experimental conditions was found to be good fit.

- The above findings clearly indicate that the SIP Waste has good potential for being utilized as an adsorbent in the heavy metal removal process from waste waters.

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